THE BOOK WAS DRENCHED

LIBRARY ANDU_172731 ANDU_172731 ANDU_172731

WATTS' DICTIONARY OF CHEMISTRY

VOL. III.

PRINTED BY

SPOTTISWOODE AND CO LTD COLCHEF LS

LONDON AND ETON

WATTS

DICTIONARY OF CHEMISTRY

REVISED AND ENTIRELY REWRITTEN (IN 4888)

ВY

H. FORSTER MORLEY, MA, D.Sc

FELLOW OF UNIVERSITY COLLEGE, LONDON AND FORMERLY PROFESSOR OF CHEMISTRY
AT QUEEN'S COLLEGE LONDON

AND

M. M PATTISON MUIR, M.A.

FELLOW AND PRÆLECTOR IN CHEMISTRY OF GONVILLE AND CAIUS COLLEGE, CAMBRIDGE

ASSISTED BY EMINENT CONTRIBUTORS

IN FOUR VOLUMES

VOL III

NEW IMPRESSION

LONGMANS, GREEN, AND CO.

80 PATERNOSTER ROW, LONDON

NEW YORK, BOMBAY, AND CALCUTTA

1912

di rights reserved

INTRODUCTION

TO THE ARTICLES RELATING TO ORGANIC CHEMISTRY

The names used we denote ring formulæ are given below for convenience of reference

Since the publication of the last volume I have been assisted in the work of reading and making abstracts of original memoirs by Drs T Cooksey, T A Lawson, Samuel Rideal, Messrs J Wilkie, G N Huntly, J T Norman, and D A Louis I have also been assisted by Mr Arthur G Green and Mr Cecil W Cunnington in the work of revising the proof sheets I have great pleasure in thanking these gentlemen for the energetic and efficient manner in which they have carried out their share of the work

H I ORSTER MORLEY

Nomenclature of Ring Formulæ

Hydrocarbons

$_{ m CH}<_{ m CH_2}^{ m CH_2}$ Trimethylene	C _v H ₄ <ch>CH Indonaphthene</ch>
CH < CH > CH2 Tetramethylene	CH≤CH CH Tetramethenyl
CH CH ₂ Pentamethylene	CH CH CH Pentamethenyl hydride

Nitrogen compounds					
NH <ch ch="" pyrrole<="" th=""><th>⁄ ен сн Сн сн}сн</th><th>Pyruline</th></ch>	⁄ ен сн Сн сн}сн	Pyruline			
NH<\\ H \ Pyrazole	л ≷ <mark>СН СН</mark> >СН	P pida-ine			
NH CH CH Gli oxalini	/≪CH CH >/	Pyra≠ine			
N CH N Metapyrazole	z ∉ CH CH SCH	Purimia ie			
NH CHN or CHN True ole	$\gamma \leqslant_{\mathrm{CH}}^{\mathrm{CH}} \gamma \geqslant_{\mathrm{CH}}$	Tria~oline			
NH N CH Osotriazele	/ <pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre>/<pre< th=""><th>Osotetra_ole</th></pre<></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre>	Osotetra_ole			
NH CH N Tetrasole	$C_{\circ}H_{\circ} <_{N=CH}^{CH}$	Quinoline			
$C_{b}H_{4} < \frac{CH}{NH} > CH$ Indole	C H' <ch n<br="">CH CH CH</ch>	Isoquinoline			
C _e H ₄ NH Indazine	$C^{e}H^{4} \leq \frac{N}{N} CH$	Quinoxalıı c			
C _s H ₄ < CH > N Psoudo indazino	C H'<_CH \	Q una [®] oline			
C,H, <n, acruline<="" th=""><th>C,H,<n=n< th=""><th>Cinneline</th></n=n<></th></n,>	C,H, <n=n< th=""><th>Cinneline</th></n=n<>	Cinnelin e			
C,H, No O,H, Phenasine					

INTRODUCTION.

Oxygen compounds

Oxygen compounds						
O CH CH Furfurane	O CH CH CH Furidane					
O CH N Oxazole	•O CH CH NH Pyroxasine					
O CH CH Iso oxazole or Isoxazole	C _s H ₄ $<$ NH CH Quinoxaz·ne					
C _e H. < CH Coumarons	C _a H ₄ C _{NH} C _a H ₄ { Phenoxarine or Phen azoxine					
CO NH Carbizine						
Sulphur c	ompounds					
SCH CH Throphene	S <ch .="" mizole<="" n="" td=""></ch>					
S CH CH C = C Throphthene S CH CH	S <ch n="" orazthrole<="" td=""></ch>					
C.H. CH C.H. SCH { Methenyl anudo phenyl mer captan	C _s H ₄ <nh>C_sH₄ Imido di phenyl sulphide</nh>					

INITIALS OF SPECIAL CONTRIBUTORS

HEV	H E ARMSTRONG, Ph D, FRS, Professor of Chemistry in the City and Guild- Central Institution Contributes Isomerism
D C	DOUGLAS CARNEGIE Esq, MA, formerly Demonstrator in Chemistry, Gonulle and Caius College, Cambridge Contributes Periodic Law
и с	WILLIAM CROOKES Esq, FRS Contributes METALS, RABE
C F C	C I CROSS, Esq, Consulting Chemist Contributes Lignone
ΙΓ	L FLETCHER, MA, FRS, Keeper of the Mineralogical Department, British Museum Contributes Mineralogical Chemistry
N D H	W D HALLIBURTON, MD, BSc, FRS, Professor of Physiology at King's College, London Contributes Milk and Muscle
A k H	A h HUNTINGTON Ph D, Professor of Metallurgy, King's College, London Contributes Metallurgical Chemistry
A H	ARTHUR HUTCHINSON MA PhD, Demonstrator in Chemistry, Gonville and Caus College, Cambridge Contributes Isomorphism
I R J	FRANCIS R JAPP, MA, PhD, FRS Professor of Chemistry in the University of Aberdeen Contributes Ketones and Lepiden
S R	SAMULI, RIDEAL, Dec. Lecturer on Clemistry at St George's Hospital Medical School Contributes Paraffer and Petroleum
W A S	W A SHINSTONE, Esq., Lecturer in Chemistry at Clifton College Contributes Ozone
T A W	WILLIAM A TILDEN, DSc, FRS, Professor of Chemistry at Mason College, Bit mingham Contributes Pentinene
JJT	J J THOMSON, MA, FRS, Professor of Experimental Physics in the University of Cambridge Contributes Molecular constitution of Bodies, theories of

Articles by Mr MUIR are initialed M M P M

ABBREVIATIONS.

I JOURNALS AND BOOKS

When an author has been mentioned in an article, he is usually referred to thereafter in that article by his initial only

```
Liebig 3 Annalen der Chemie
A
A
  A
           Annales de la Sociedad Cientifica Argentina
A Ch
           Annales de Chimie et de Physique
P Am A
           Proceedings of the American Academy of Arts and Sciences.
           American Chemical Journal
Am
Ann M
           Annales des Mines
Am S
           American Journal of Science
ACJ
           Journal of the American Chemical Society
Am Ch
           American Chemist
           American Journal of Pharmacy
Am
 Pharm
An
           The Analyst
A Ph S
           Proceedings of the American Philosophical Society.
ir N
           Archives no erlandaises-The Hague
4 ad
           Mémoires de l'Academie des Sciences
Ar Ph
           Archiv der Pharmacie
A) Sc
           Archives des Sciences phys et nat
B
           Berichte der deutschen chemischen Gesellschaft.
           Reports of the British Association
BA
Rl
           Bulletin de la Société chimique de Paris
B B
           Beiliner Akademie Berichte
B C
         Biedermann's Centralblatt für Agricultur Chemie
B J
           Berzehus' Jahresberichte
B M
           Berliner Monatsberichte
  S Mem
           Memoirs of the Chemical Society of I ondon
C
  J
           Journal of the Chemical Society of London
\boldsymbol{C}
C J Proc
           Proceedings of the Chemical Society of London
_{C}^{C}
  \frac{N}{3}
           Chemical News
           Comptes rendus hebdomadaires des Sciences de l'Académie des Sciences
               Paris
C
           Chemisches Central Blatt
D P J
           Dingler's polytechnisches Journal
           Fresenius Zeitschrift für analytische Chemie
Fr
G
           Gazzetta chimica italiana
G
  A
           Gilbert's Annalen der Physik und Chemie
H
           Hoppe Seyler's Zeitschrift für physiologische Chemie
Į
J
           Proceedings of the Royal Irish Academy
           Jahresbericht über die Fortschritte der Chemie und verwandter Theile
                anderer Wissenschaften
JCT
           Jahresbericht für Chemische Technologie
J M
           Jahrbuch für Mineralogie
           Journal de Physique et des Sciences accessoires
  de Ph
J Ph
           Journal de Pharmacie et de Chimie
  \frac{pr}{Th}
           Journal fur praktische Chemie
           Jahresbericht über Thierchemie
JR ?
           Journal of the Russian Chemical Society
JZ
LV
M
           Jenaische Zeitschrift für Medicin und Naturwissenschaft
   V
           Landwirthschaftliche Versuchs Stationen
           Monatshefte für Chemie und verwandte Theile anderer Wissenschaften
M S
           Le Moniteur Scientifique
Mém
           Mémoires de la Société d'Arqueil.
           Mémoires couronnés par l'Académie de Bruxelles
Mem B
  VOL II
```

```
Nature.
   Ed P.J.
New Edinburgh Philosophical Journal.
             Neuer Jahresbericht der Pharmacie
Neues Repertorium für die Pharmacie.
             Neues Journal von Trommsdorff
             Philosophical Magazine
             Poggendorff's Annalen der Physik und Chemie
             Beiolatter zu den Annalen der Physik und Chemie.
             Pfluger's Archiv für Physiologie
             Proceedings of the Royal Society of Edinburgh.
             Pharmaceutical Journal and Transactions
             Pharmaceutisches Central Blatt
             Proceedings of the Royal Society
Proceedings of the Royal Institution of Great Britain.
             Pharmaceutische Zeitschrift für Russland
             Recueil des travaux chimiques des Pays Bas
             Repertorium fur die Pharmacie
             Quarterly Journal of Science
             Schweigger's Journal der Physik
             Scherer's Journal der Chemie
             Journal of the Society of Chemical Industry
 Sitz W
             Sitzungsberichte der K. Akademie zu Wien
Sitz W
T or Tr
T E
W
W J
Z
Z B
Z f d g
             Transactions of the Royal Society
             Transactions of the Royal Society of Edinburgh.
             Wiedemann's Annalen der Physik und Chemie
             Wagner's Jahresbericht
             Zeitschrift für Chemie
             Zeitschrift für Biologie
   f d g
Natur-
             Zeitschrift für die gesammten Naturwissenschaften.
   wiss
   K
             Zeitschrift für Krystallographie und Mineralogie
 \bar{z}
   P
       \boldsymbol{C}
             Zeitschrift für physikalische Chemie
 Bn
             Handbuch der organischen Chemie von F Beilstein, 2te Auflage
 EP
             English Patent.
 GP
             German Patent
 Gm
             Gmelin's Handbook of Chemistry—English Edition
             Gmelin-Kraut Handbuch der anorganischen Chemie
 Gm - K
             Traité de Chimie organique par Charles Gerhardt
Lehrbuch der organischen Chemie; von Aug Kekulé
 Gerh
 K
 G O
             Graham Otto Lehrbuch der anorganischen Chemie [5th Ed]
 Stas,
             Stas' Recherches, &c
                                                 Aronstein's German translation is re
   Rech
             Stas' Nouvelles Recherches, &c
                                                     ferred to as Chem Proport
 Stas,
  Nouv
 Th
             Thomsen's Thermochemische Untersuchungen
```

II TERMS AND QUANTITIFS, &c , FREQUENTLY USED

```
Water, e.g NaOHAq means an aqueous solution of caustic sods
aq
A'
A''
                  18 parts by weight of water
                  Residues of mono, di, and tri basic acids Thus, in describing the salts of a monobasic acid NaA', CaA'<sub>2</sub>, AlA'<sub>2</sub> may be written, HA' standing for the acid For a dibasic acid we should write Na<sub>2</sub>A'', CaA'', Al<sub>2</sub>A''<sub>3</sub> &c Stand for bases of the ammonia type, in describing their salts Thus the
B' B" &c
                          hydrochloride would be B'HCl or B"2HCl, according as the base is
                          monacid or diacid, &c
                   Concentrated.
conc
dıl.
                   Dilute
                  gram
mgm.
                  milligram.
                  millimetre.
mm
mol
                  liquid nearly, or quite, insoluble in water
oil
                  precipitate
pp
to ppt
                  to precipitate.
                  precipitating
ppg
ppd.
                  precipitated.
```

```
soi
             soluble in.
             ınsoludle ın
very easıly
ınsol
v e sol
             very
v sol
                             soluble in.
             moderately
m so
             slightly
sl. soi
la la v
             very slightly
v
             see
cf
             compare
c
             about
  ٥١
             a melting point
             a builing point
Η
Λι∾
             Hardness (of minerals).
             Atomic weight
Mol w or
             Mole ular weight.
  M w
D
             Densi
             corrected
ecor
              uncorrected
uncor
ı V
             in vapour
              vapour density, i c density of a gas compared with hydrogen or air
V D
SG
              Specific gravity compared with water
5 G 19
5 G 14
8 G 14
                               at 10 compared with water at 0°
                                " 15°
                                                              ,, 4°
                         ••
                                ,, 12°, compared with water of which the temperature is
                 not given
 SH
              Specific heat
 SHv
                            of a gas at constant volume
 SHp
                                                   pressure
              Quantity of heat, in gram units, produced during the complete com-
bustion of the mass of a solid or liquid body represented by its
 HC
                   formula, ...ken in grams
              Heat of combustion in gram units of a gram molecule of an element or
 HCv
                   compound, when gaseous, under constant volume
 HCp
HF
              The same, under constant pressure
              Quantity of heat, in gram units, produced during the formation of the mass of a solid or liquid body represented by its formula, taken in
                   grams, from the masses of its constituent elements expressed by
                   their formulæ, taken in grams
 HF v
              Heat of formation of a gram molecule of a gaseous compound from the
                   gram molecules of its elements under constant volume
 HFp
HV
              The same, under constant pressure
              Heat of vaporisation of a liquid, i.e. gram units of heat required to change
                    a gram molecule of the liquid compound at B P into gas at same
                    temperature and pressure
               Thermal conductivity (unit to be stated)
 S V
               Specific volume, or the molecular weight of a gaseous compound divided
                   by the SG of the liquid compound at its boiling point compared with
                    water at 4°
 8.V S
               Specific volume of a solid, or the mass of the solid expressed by its
                    formula, taken in grams, divided by its S G
 EC
               Electrical conductivity (the unit s stated in each case)
               Coefficient of expansion (between 10° and 20°)
  CE (10°
  • to 20°)
                          of a gas = volume dissolved by 1 volume of water of a liquid or solid = number of grms dissolved by 100 grms of water. In both cases the temperature
  8
               Solubility in water
  B (alco
    hòl)
                                       18 stated
               Index of refraction for hydrogen line \beta
  μ,
  μ<sub>υ</sub>, &ο
R<sub>υ</sub> y
               " ,, sodium ,, D, &c
Molecular refraction for sodium light, se index of refraction for line D
                    minus one, multiplied by molecular weight, and divided by S G at 15°
                    compared with water at 0°
               The same, S.G being determined at 15°-20° and referred to water at 4°
  R,
  R_{\infty}
               The same for line of infinite wave length, index being determined by
                  • Cauchy's formula (Bruhl's R.)
  [a]<sub>D</sub>
               Specific rotation for sodium light
                                  ,, neutral jnt [a] = \frac{100}{p} \times \frac{a}{d} a = \text{obsefved rotation for}
  [=]
                    100 mm of liquid. d=8 G. of liquid. p=no of grammes of activa substance in 100 grammes of liquid
```

```
m \times a
M M
              Molecular magnetic rotatory power = \frac{m_{i}}{l - \alpha' \times m'}, where m = molecular
                   weight of the body of SG = d, \alpha = an de of rotation under magnetic influence, \alpha' = angle' of rotation of water under same influence, and
                   m' = molecular weight of water (18)
              Acetyl C.H.O
Ac
\mathbf{B}\mathbf{z}
              Benzoyl C,H,O
Су
              Cyanogen CN
Et
              Ethyl C.H.
Me
              Methyl CH.
Ph
              Phenyl C.H.
                                                    ın formulæ
\mathbf{Pr}
              Normal Propyl CH<sub>2</sub> CH<sub>2</sub> CH,
Isopropyl CH(CH<sub>3</sub>)
\mathbf{p}_{\mathbf{r}}
R, R' etc
              Alcohol radicles or alkyls
prim
              primary
sec
              secondary
tert
              tertialy
n
              normal
m, o, p
             meta- ortho-para
c
             consecutive
ı
             ırıegular
s
             symmetrical
и
             unsymmetrical,
ψ
             pseudo
ν
             attached to nitrogen
             Employed to denote that the substituent is attached to a carbon atom
                   which is next, next but one, or next but two, respectively, to the terminal carbon atom. The end to be reckoned from is determined
a
В
γ
                   by the nature of the compound Thus CH<sub>3</sub> CHB<sub>1</sub> CO<sub>2</sub>H is a bromo
                   propionic acid
              denotes that the element or radicle which follows it is attached to a ter
                   minal carbon atom
\sigma, \beta, \gamma, \text{etc}
              indicate position in an open chain, only
1,2,3, etc
              indicate position in a ring only
(\alpha), (\beta),
              Used when a, B, &c are employed in a sense different from the above,
  etc
                  eg (a) di biomo camphor
             Baeyer's Nomenclature
(B)
                  benzene ring
                   pyridine ring
Thus (B 13) dichloroquinoline, means a meta dichloroquinoline in
(Py).
                   While (Py 13) dichloroquinoline, means a similar body, only the
                   chlorine atoms are in the pyridine ring. The numbers are counted
                   from two carbon atoms which are in different rings, but both united
                   to the same carbon atom
(A).
             denotes the central ring in the molecule of anthracene, acridines, and
es0
             means that the element or radicle it precedes is in a closed ring
ero-
                                                                     not in a beuzene ring
allo
              denotes isomerism that is not indicated by ordinary formulæ, thus maleic
                   acid may be called allo-fumaric acid
thio
              denotes displacement of oxygen by sulphur
sulpho
                       the group SO,H, except in the word sulphocyanide
sulphydro.
                      the group SH
             Tribromonitrobenzene sulphonic acid [12345] means that the three
                   bromines occupy positions 1, 2, and 3, the nitro group the position 4,
                   and the sulpho group the position 5
```

* Denotes that the formula to which it is affixed has not been determined by analysis. But it by no means follows that formulæ without this mark are those of analysed compounds

All temperatures are given in degrees Centigrade unless when specially stated otherwise

Wave lengths are given in 10 7 mm

Formulæ, when used instead of names of substances, have a qualitative meaning only

Thomsen's notation is used in thermochemical data

DICTIONARY OF CHEMISTRY.

INDIGO CARBOXYLIC ACID v Indigo INDIGO-CARMINE . INDIGO IKDIGO-SULPHONIC ACID v Indigo INDIGOTINE v Indigo INDIGO-WHITE v Indigo INDILEUCINE v Indigo

INDIN C16H10N2O2 Formed by the action of potash upon isatyde, thio isatyde, or di thio isatyde, formed also by heating isatan (Laurent, A Ch [3] 3, 471) Obtained also by boiling a solution of dioxindole in glycerin for a long time (Knop, Z 1865, 273) Deep rose coloured pow der or minute needles Insol water, v sl sol alcohol and ether Dissolves in H2SO, forming a red solution, whence it is ppd unchanged by water A solution in concentrated alcoholic KOH deposits black crystals, apparently either C₁₆H₉KN₂O₂ or, more probably, potassium indate C16H16KN2O3

Di bromo-indin C16HBr2NO Formed by the action of bromine on indin or on di thio isatyde (Laurent) Formed also by heating di bromo isatvde at 220° (Erdmann J pr 22, 265)

Violet black powder, sl sol alcohol

Di chloro-indin C₁₆H₂Cl N₂O₂ Obtained by heating di chloro isatvde either alone or with alcoholic potash (E) Dirty violet powder, insolwater, alcohol, and HClAq Forms a vellowish solution in KOHAq from which HCl ppts vellow flakes

Tetra caloro indin C16H2Cl4N2O Formed by heating di chloro isatyde either with alcoholic potash or alone below 200° (E) Dirty violet

powder

Di nitro-indin C₁₆H₄(NO₂)₂N O₂ Formed by boiling indin or hydrindin with HNO₃ (L) Formed by Bright violet powder, insol water, v sl sol al cohol and ether Forms a dark brown solution

in KOHAq

Indin di-sulphonic acid C16H, (SO,H)2N2O2? Formed by oxidising hydrindin di-sulphonic said with IINO2, with K2FeCy4, with NaOCl, or even by exposing it in alkaline solution to the air (G a A Schlieper, A 120, 24) Red deliquescent crystals, v sol water, sl sol alcohol, insol ether Its solution dyes silk and wool scarlet nium sulphide reduces it to hydrindin di sul phonic acid. It forms a purple solution in KOHAq, and on warming the solution it becomes pale red, probably through assimilation of water On adding HCl to the pale red sol tion a yellow pp is formed (C₁₈H₁₆(SO₃H)₂N₂O₅?), which, when heated, quickly changes to indin disulphonic, acid Salts—K,A'5aq lustrous red needles—Ag,A'' bulky brown needles—BaA''2aq slender dark reddish-brown needles or crimsch berg (c. 1 p. c.), also from Durham (Flight, B. 10, Vor. III

powder M sol water, insol BaCl, Aq, alcohol

and cold HClAq

Hydrindin C₁₂H₂₂N₄O₅? Formed by the ac tion of alcoholic potash upon indin, isatyde, thio isatyde, or di thio isatyde (Laurent A Ch [3] 3, 475) White, or pale yellow powder or needles (from alcohol), insol water, sl sol boiling Boiling HNO, converts it into a violet alcohol powder Hydrindin dissolves in warm aqueous KOH, and on cooling there separate pale vellow needles of a salt C, H, KN,O, 3aq, which is decomposed by washing with water, leaving hydrindin

Hydrindin disulphonic acid, so called, C_{1a}H₁ (SO₃H)₂N₂O₂? Formed by the action of ammonium sulphide on indin sulphonic acid or on isatin sulphonic acid (G a A Schlieper, A 120, 20) Colourless radio crystalline mass, which becomes reddish when exposed to Lar V water, m sol alcohol, insol ether In alkaline solution it is oxidised by air to indin sulphonic acid -BaA'4aq white scales, v sol water, v sl sol BaCl, Aq

Leucindin disulphonic acid

C₁₆H₁₆(SO₃H) N₂O₄ Formed by boiling the preceding with baryta water (G a A Schlieper, A 1'0, 33) White crystalline mass, v sol water, sl sol alcohol Not reddened by the action of air on its alkaline solutions. On evaporating with HCl Aq there is formed indin disulphonic acid—BaA" 5aq colourless crystals Its solution is not ppd by AgNO, till NH,Aq is added

INDIPURPURIN is identical with Indirubin v Indigo

INDIRETIN v INDIGO INDIRUBIN v Indigo

INDIUM In At w 1134 Mol w unknown, as V D of element has not yet been de-[176°] (Winkler, J pr 102, 273) termined S G $^{20.4^{\circ}}$ 7 11 to 7 147 (Reich a Richter, J pr 93, 480), 150 7 362, 16 90 7 421 (Winkler, J pr 95 414, 102, 273) SH (0° to 100°) 05695 (Bun sen, P 141, 1) CE (0° to 100°) 0000459 (Fizeau, C R 68, 1125) Characteristic lines in emission spectrum 4510 2,4101 3, 4071 6, 4032 7, 3452 8, 3834 7, 3257 8, 3255 5, 3038 7, 3008, 2982 3, 2940 8, 2889 8, 2559 5, 2527 1, 2351 3, 2306 9 (Hartley, T 1884 102)

The observation of two indigo blue lines in the spark spectrum of a specimen o. the sincblende of Freiberg in 1863, led Reich a Richter

INDIUM

2054), and from Bohemia (Kachler, J pr 96, 447), in some Italian galenas (Denegri, B 11, 1249), in various zinc ores (Tanner, J 1874 1227), in the fumes from zinc-ovens (Böttger, J pr 98, 26), ir some tungsten ores (Hoppe-Seyler, A 140, 247)

Preraration -Indium is more readily prepared from zinc which has been made from indium containing blendes than from zincblende itself The zinc is treated, for some days at the ordinary temperature, or for a shorter time at boiling temperature, with so much dilute H.SO.Aq or HClAq that a small quantity remains undissolved, the residue contains In, with some Zn, and Pb, Cu, Cd, As, and Fe There are many methods for obtaining In from this residue, that of Bayer (A 158, 372) is simple, and yields very pure in The residue is washed, treated with a few drops of dilute H2SO, Aq (to remove any basic Zn salts), again washed enoroughly with hot water, dissolved in HNO,Aq (any SnO, which may be present is allowed to remain), evaporated with excess of H2SO, until all HNO, is removed, and treated with water, the solution now contains sulphates of In and the other metals which may be present, but the greater part of the PbSO4 remains insoluble Large excess of NH,Aq is added, whereby hy droxides of In and Fe are ppd with small quan tities of hydroxides of Zn, Cd, Pb, and Cu, the pp is well washed and dissolved in the smallest possible quantity of HClAq, the solution is boiled after addition of NaHSO, until the smell of SO₂ is a most cone, a basic sulphite of In, 2In,O, 3SO, is thus ppd as a fine crystalline The pp is free from salts of Cu, Zn, and Cd If much Fe should have been present in the original Zn, small quantities of Fe salts may be ppd by the action of the air during filtration, in this case ppn should be conducted in CO2, or the pp should be dissolved in NaHSO Aq, and re ppd by boiling may contain Pb salts and traces of alkali, it is dissolved in SO₂Aq in which Pb sulphite is in soluble, after filtration In sulphite is ppd , free from Na salts, by boiling (cf Winkler, J pr 102, 278, Böttger, J pr 98, 26, R E Meyer, A 150, For methods of preparing In from zincblendes v Reich a Richter, J pr 89, 441, 90, 175, 93, 480, Weselsky, J pr 94, 443, Richter, J pr 94, 414, Stolba, D P J 198, 223) The ppd basic In sulphite may be dissolved in H.SO.Aq, after boiling off SO, addition of NH,Aq ppts InO,H,, which when strongly heated yields In₂O, In is obtained from the oxide (1) by heating in a stream of pure H, (2) by mixing with pure C, and heating to a very high temperature, (8) by heating with an equal weight of Na cut in small slices, under a layer of fused NaCl in a porcelain crucible placed in a larger Hessian crucible, decomposing the alloy of Na and In so formed by water, and melting with Na₂CO₂ (Winkler, J pr 102, 275) Böttger (J. pr 107, 39) recommends to ppt In from solutions in H SO, by placing a stick of pure Zn in the liquid, he washes the ppd metal with water, presses it with the finger, then between paper, and when quite dry fuses it under dry

Properties -A silver white, lustrous, ductile metal; softer than lead, leaves a mark when

rubbed on paper Non-crystalline Electronegative ... Zn and Cd , much less volatile than these me cals . Unchanged in air at ordinary temperateres, but burns to In,O,, with blueviolet flame and brownish fumes, when strongly heated in air Combines directly with Cl, Br, I, and S when heated Boiling water is not de composed by In Soluble in dili e acids with evolution of H and formation if salts In.X. where $X = SO_4$, $2NO_3$, &c

The at w of In has been deermined (1) by synthesis of In₂O, from an (Acich a Richter, J pr 92, 484, Winkler, J pr 94, 8, 102, 282, Bunsen, P 141, 28), (2) by analyses of In₂S, (R a R, lc) (8) by decomposing NaAuCl, by In, and determining the Au (Winkler, J pr 102, 212), (4) by determs ng the VD of InCl_{st}, InCl_{st}, and InCl (Nilson a Pettersson, C I 53, 814), (5) by determining the S H of In (Bunsen,

P 141, 1)

The atom of In appears to be monovalent (in InCl), divalent (in InCl2), and trivalent (in InCl,), in gaseous molecules, as the lower chlorides are decomposed by water with forma tion of In and InCl, it is probable that in solu tions of its haloid compounds the atom of in is directly combined with at least three monova lent atoms

In is distinctly metallic, with acids it evolves H and forms salts A few basic, and some double, salts are known In forms an ammonia alum InO, H, rCacts towards acids as a salt form ing hydroxide In is closely related to Al and Ga, less closely to Tl, it is also related to the other earth metals Sc, Yt, La, and Yb (v EARTHS, METALS OF THE, vol 11 p 424) The investigation of In compounds is as yet far from complete

Detection and Estimation -In salts colour the flame blue violet Hoppe Seyler (A 140, 247) boils c 1 gram of an In ore with aqua regia, neutralises by soda, filters, adds Na acetate, and ppts by H2S, he dissolves the pp in acid, and reppts, the In2S, is then tested in the flame after moistening with HClAq The spectral lines 4510 2 and 4101 3 are very characteristic Boiling with NaHSO, causes ppn of t, fine crys talline pp 2In,O, 3SO, 8H,O, this salt is used for the estimation of In

Indium bromide InBr. White crystalline tablets, v sol water, formed by heating In in a White crystalline stream of CO, charged with Br, and subliming (R Meyer, A 150, 429) VD not determined Indium chlorides In combines with Cl in

three proportions, forming InCl, InCl,, and

Indium monochloride InCl Mol w 148 77 V D at c 1100°-1400° = 78 16 (Nilson a Pet tersson, C J 53, 821) Obtained as a reddish black, vitreous, radiated, crystalline mass, by distilling InCl. (q v) on to In (rather more than the calculated quantity), heating for a little in a sealed tube, and distilling in a stream of CO. (N a P, l.c.) When melted InCkforms a darkred liquid, in thick layers appearing almost Deliquescent, gradually decomposes in black

moist air, and quickly in water, to In and InCl.
INDIUM DICHLORIDE InCl. Mol w 184 14
VD at 1000°-1400°-99 62 (Nilson a Petters Non, C J 58, 820) White radiated crystals, obtained by heating In to its melting point in a current of dry HOl free from air until an amberINDIUM.

coloured liquid is obtained, and removing any adhering HCl by heating in dry as free CO_x. Unchanged in dry air, but deliquese p in ordinary air Decomposed by water to in a id InCl. Aq

(N a P, lc)

INDIUM'TRICHLORIDE InCl. Mol wi 219 51 V D at c 850°=106 9 (Nilson a Pettersson, C J 53, 818), at bright red heat V D = 113 88 (V a objection at 140°, at c 600° volatilisation is slow and V DA is rather higher than that calculated for Incl., the normal V D is attained between 600° and 850°, at temperatures towards 1000' dissociation begins, probably into Cl and InCl. or InCl (N a Polc) InCl. is prepared by heating In or a mixture of In2O, with C, in a stream of dry Cl Vilson a Pettersson heated molten In in day air free HCl, and then gently heated the InCl, thus formed in air free, dry, Cl, and finally 'istilled in a current of dry, air free, CO, White, lustrous tablets, deliquescent, sol in water with production of heat, the solution may be evapo rated on a steam bath almost unchanged, but at higher temperatures decomposition probably w'th production of oxychlorides

InCl, combines with KCl NaCl, LiCl, and PtCl, to form crystalline double salts (R Meyer, A 150, 144, Nilson, B 9, 1059) The compound 2InCl, 6KCl 3H.O separates in quadratic crystals from a solution of the mixed salts in proper

proportions on evaporation

Indium cyanide v vol 11 p 332

Indium hydrosulphide The white pp pro duced by adding NH, sulphide, or kHS, to solu tion of an In salt, after addition of tartaric acid and NH, Aq, is probably a hydrosulphide, when dried, H2S is evolved and In2S, remains (R Meyer, A 150, 429)

Indium hydroxide v Indium oxides and

hydroxide

Indium iodide InI, VD not determined Yellow, crystalline, very hygroscopic, may be distilled in dry CO₂, easily melted to a dark reddish brown liquid. Prepared by heating In

two oxides, InO and In O,, the VD of neither has been determined, the existence of inter mediate oxides is probable In₂O₃ forms at least one hydrate In2O, 3H2O The oxides are basic, only salts corresponding to In,O, have dissolve in dilute acids without decomposition

into In and In,O,

INDIUM MONOXIDE INO Mol w unknown, as the oxide has not been volatilised Obtained by heating In,O, in H at c 300° until the oxide becomes almost black and water is no longer evolved Forms a light, loose, powder, which quickly oxidises to yellow In₂O₃, if brought into air before it is quite cold Very pyrophoric InO is changed by conc HNO₂Aq to In3NO₂ with evolution of NO, dilute acids dissolve it slowly without apparent formation of In₂O₂ or In (Winkler, J pr 94, 1, 95, 414, 98, 344, 102,

INDIUM SESQUIORIDE IngO, Mol. w unknown as the oxide has not been volatilised SG 7179, SH (0°-100°) 0807 (Nilson &. Pettersson, B 18, 1459) Obtained by ppg solution of an In salt by NH Aq, washing and host-

ing the pp, or by heating In talfull redness in air, also by strongly heating In carbonate or nitrate A yellow powder, becomes brown on heating but yellow again when cold (It is doubtful whether pure In₂O₃ is yellowish or white) Very infusible, reduced to metal by heating with C, or in H, or with Na, reduction in H begins at c 190°-200°, and at c 300° Ino is formed (v supra) Soluble, in soids, quickly on heating, forming salts In. 3X (X-SO, 2NO,

Oxides intermediate between InO and In.O. possibly exist By heating In₂O₂ in H to c 200°, a greyish blue body is obtained probably In.O. at c 230° a green substance, probably In O.

remains (Winkler, lc)

INDIUM HYDROXIDE InO,H, or In,O, 3H,O Formed by ppg a solution of an in salt by NH, Aq, washing the pp and drying at 100° The pp by NH,Aq is gelatinous and resembles AlO,H, in air it dries to horny semitransparent lumps Insol in NH,Aq, easily sol in KOHAq or NaOHAq, dissolves in acids to form salts $In_2 dX$ (X = SO_4 , $2NO_3$, &c) A series of very unstable hydrates of In.O. probably exists (cf Carnelley a. Walker, C J 53, 88) Indium exybromide The white amorphous

solid formed by heating In,O, in Br vapour is probably an exybromide, this substance is said not to be decomposed by heating with acids or

alkalıs (R. Meyer, A. 150, 137)

Indium oxychloride When InCl.Aq 18 boiled down to dryness, the white residue is pro-

bably an oxychloride

Indium salts Not many salts of In have been isolated and examined. They are obtained by dissolving In or InO.H. in acids, and evaporating, and in some cases by ppn from other In salts The chief salts are the carbonate, in solution nitrate, sulphate, and a basic sulphite (v Car BONATES NITRATES, &c) The sulphate forms an ammonia alum, In, (SO,), (NH,), SO, 24H,O, but with K₂SO, and Na, SO, it forms double sul phates In₂(SO₄), K₂(Na) SO₄ 8H₂O

in I vapour (R. Meyer, A. 150, 144, 429)

Indium sulphide In, S. Mol w unknown
Indium oxides and hydroxide In forms as compound has not been gasined. Obtained by ppg a neutral or feebly acid solution of an In salt by H.S. and drying the pp , also by heating together In and S. or In.O. and S. A yellowishgrey solid If In,O, is heated with S and Na,CO, and the fused mass is treated with water, In.S. been isolated, although the lower oxide is said to remains as lustrous tablets resembling mosaic gold (Winkler, lc) In2S, is infusible, with acids it gives In salts and H.S (Reich & Richter, lc) Heated in air it is burnt to In₂O, According to Winssinger (Bl (2) 49, 452) In₂S, is obtained in aqueous solution in a colloidal form, by passing H.S into InO,H, suspended in water, the dark yellow liquid thus obtained can be freed from H.S by boiling, it is coagulated by acetic acid and also by salts For reactions of alkali sulphides with In salts v R Meyer, lc

Potassium, and sodium, indium sulphides, K.S In.S., Na.S In.S. Formed by fusing together 1 pt In,0,, 6 pts S, and 6 pts K,CO, or Na,CO, The K salt remains as hyacinth red quadratic tablets on harvisting the fused mass with water, the Na salt goes into solution and separates on standing as Na,In,S, H,O which on drying gives Na,In,S, (R. Schneider, J pr [2] 9, 209)

M M P M

INDOGEN & INDOXYL INDOGENIC ACID v Indoxylic acid INDOGENIDE OF BENZOIC ALDEHYDE

C1.H11NO 16 C6H4 CONH CH.C6H, B nsyl-

[176°] Obtained by heating ıdene ψ-ındoxyl indoxylic acid with benzaldehyde (Baeyer, B 16, Long flat orange needles Sol alcohol and chloroform to yellowish red solutions, which have a yellowish green fluorescence In H,SO and strong HCl it dissolves with a deep red colour, in alcoholic KOH with a greenish blue, which gives the indigo spectrum
(a)-INDOGENIDE OF \(\psi \) ISATIN is INDIRUBIN

β)-Indogenide of ψ isatin is Indigo

Indogenide of ethyl ψ isatın 18 Ethyl ındı rubin v Indigo

INDOGENIDE OF p-NITRO-BENZALDE HYDE C₁₅H₁₀N₂O₃ 18

CH CH (NO) p Nitro-benzylidene-v-indoxyl [273°] Formed by adding an acetic acid solution of p nitro benzaldehyde to an aqueous solution of indoxyl acidined with Red needles (Baever, B 16, 2199)

INDOGENIDE OF PYRUVIC ACID C,H,NO, $C_{\bullet}H_{\bullet} < CO > C CM_{\bullet} CO_{\bullet}H$ [197°] pared by adding HCl to an aqueous solution of indoxyl and pyruvic acid (Baeyer, B 16, 2199) Easily soluble in alcohol and Red needles acetone Dissolves with a red colour in alkalis, with a blue colour in conc H2SO,

INDOINE v Indigo

small quantity in human excrement (Brieger,

J pr [2] 17, 133)

Formation -1 By passing the vapour of oxindole over heated zinc dust (Baeyer, A 140, 295, Suppl 7, 56, Engler a Janecke, B 9, 1411) -2 By distilling with zinc dust the yellow product of the action of tin and HCl on indigo (B) -3 By fusing o nitro cinnamic acid with KOH and iron filings (Baeyer a Limmer ling, B 2, 679, Z [2] 6, 213, Beilstein a Kuhl berg, A 163, 141) -4 Formed to the extent of 5 pc in the passage through a red hot tube of di ethyl o-toluidine, in less quantity from di methyl-o-toluidine, in small quantity frommethyl ethyl aniline, ethyl acetanilide, and di ethyl aniline, and in trace only from ethylaniline when subjected to like treatment (Baever a Caro, B 10, 692, 1262) — 5 By digesting albumen with pancreas and water at 40° to 45° for several days (Nencki, B 8, 336, Kuhne, B 8, 206) According to Harris and Tooth (JPhysiol 9, 220) its formation is due to a special micro-organism - 6 By distilling albumen (1 pt) with KOH (8 pts), the yield being about 25 pc (Engler a Janecke, B 9, 1411, Nencki, J pr [2] 17, 98) -7 By distilling (3,4,1) nitro propenylbenzoic acid with lime (Widmann, B 15, 2552) 8 By boiling aniline with di chloro acetic aldehyde or with di chloro di ethyl oxide (Berlinerblau, M 8, 180) - 2. By heating ω chloro o-amide styrene with NaOEt at 165° (Lipp, B 17, 8067) - 10 Together with ethane, ethylene, and propylene, by the distillation of o cumidine

C₀H₄(NH₂)(C₂H₂) over red hot PbO (Filett, G. 13, 381) — 1 By the dry distillation of o tolyloxamic as d (Mauthner a Linda, M 7, 238) — 12 From phenyl-ethylene diamines by successions of the control of the c sive oxidation vith CrO, and distillation over zinc du.t (Prud.iomme, Bl [2] 28, 550) -18 By fusing carbostyril with potash (Mo gan, C. N. 36, 239)—14 In small quantity, b. heating the phenyl hydrazide of pyruvic acid with ZnČl, at 200° (E. Fischer, B 19, 156°) —1? By distilling calcium phenyl amido acetate with calcium formate (Mauthner a Suida, M 1., 253)

Preparation —1 By heating aniline (50g)

with an equal volume of water with inverted condenser and gradually dding di chloro ether (25 g) After boiling for an hour the excess of aniline is distilled off, ad the res due heated for 5 hours at 220° (Berlinerblau, M 8, 189) --2 By distilling a mixture of calcium phenyl amido acetate with calcium formate, extractir the distillate with ether, shaking the ether with dilute acid to remove aniline, evaporating and distilling with steam The indole is purified by conversion into the picrate The yield is 5 p c of the theoretical quantity (M a S)

Properties - Colourless lamine, m sol not water, v sol alcohol, ether, and heroin Readily volatile with steam An alcoholic solution, acidified by HCl, dyes pine wood vellow a peculiar, but not very powerful, odour a very weak base, with cone HCl Aq it forms a sparingly solubio salt, decomposed by boiling

Reactions - 1 Suspended in water and sub jected to the action of ozonised oxygen indole is converted into indigo and resinous products (Nencki, B 8, 727, 1517) Indigo appears in the urine after subcutancous injection of indole 2 Aqueous CrO, yields a bulky violet brown pp, insol other, chloroform, and benzene, sl sol alcohol, forming a red solution sol conc HClAq (L a J) - 3 Heated with MeI it gives di methyl quinoline dihydride (Ciamician a Latti, B 22, 1980) —4 When to an aqueous solution of indole there is added a few co of HClAq, and then a large quantity of fuming HNO, (previously partially freed from nitrous fumes by evaporation), a red pp is formed which may be purified by solution in alcohol and precipitation by adding ether. This substance, so cilled nitroso indole nitrate C16H13(NO)N2HNO3, forms minute red needles. v sl sol water and ether, v sol alcohol nearly insol dilute nitric acid. It detonates sharply when heated Alcoholic ammonium suiphide reduces nitroso indole mitrate to so called hy drazo indole C10H13N2 (?), which forms vellow needles, sol alcohol and ether, melting at 140° to a deep-blue mass Acids and alkalis convert it into a dark brown colouring matter termed

Picrate C_nH₂NC₆H₂(NO₂)₂OH Long red glittering needles

Acetyl derivative C.H.NAc From indole and Ac,O at 190° (Bacyer, B 12, Long needles (from water) or four sided 1314) pyramids (by sublimation)

(A)-Acetyl-indole C.H. CCO CH. Methul in 'yl ketone [190° cor] Obtained by heating indole (a)-carboxylic ac 1, prepared fr .n methylketole, with ten times its bulk of Ac2C or 7 hours at 220° (Carlo Zatti, Rend Accod 1 inc [4] 4, 184, B 22, 662) White need'ss Sublimes in colourless plates, al sol cold, v sol warm water and benzene, may be extracted from its aqueous solution by ether Gives indole when heated with cone HClAq It readily yields an oxim and an only henyl hydrazide Potash fusion converts it nto indole (8) carboxylic soid [214°] identic , with that obtained by oxidising skatole

Piorate [1834] Needles, sl. sol cold benzene

Oxim C.H.C(NOH)Me [144'-147°] White

Di-acetyl indole C.H. CH CO CH, C CO CH2 [147°-150°]

Prepared by heating indole (a)-carboxylic acid with Ac,O and separated from the preceding by its greater solubility in water containing Na, CO, and in boiling benzene (Zatti) Needles (by sublimaticn), sl sol boiling water When bo ed with aqueous kOH or K₂CO₂ it yields (B) acetyl indolc

References - Di chlobo indolp, Brazil INDOLE, METHYL INDOLF, METHYL ETHYL INDOLE, ETHYL INDOLE

Isoindole is Di PHFNIL I TRAZINE (q v) Di indole v Indoline under Indiao

Retin indole C.H. O? Obtained by treating di chloro indole (chloro oxindole chloride) with HI dissolved in HOAc passing in SO and pps, with NaOH (Bacyer, B 12, 1313) Amorphous, insol NaOHAq, v sol alcohol and ether Its solution in HOAc volatile with steam mixed with HCl colours pine wood red On dry distillation it yields indole

INDOLE (a) CARBOXYLIC ACID C,H NO, • C,H, < CH > C CO H [201°]

Formation -1 By heating the phenyl hy drazide of pyruvic ether with ZnCl, at 195° (E. Fischer, B 19, 1567, A 236, 140) -2 By fusing (a) methyl indole (methyl ketole) (1 pt) with KOH (15 pts), the acid being ppd by H2SO, from the dissolved product, the yield 18 over 50 pc (Ciamician a. Zatti, hend Accad Lanc [4:4, 746) -3 From acetyl (a) methyl - indole C.H. CH SCMe by potash fusioi (Ciamician a Magnanini, B 21, 673)

Properties - Needles (from water) M sol hot water and benzene, v sol alcohol and ether May be sublimed in plates, but suffers partial decomposition thereby At 230° it splits up into indole and CO. Pine wood acidified with HCl is not coloured yellow by it. With isatin and H2SO4 it gives a reddish violet colouration It forms a picric acid compound crystallising in slender golden needles Its Ba salt is soluble Ac₂O at 220° forms (β) acetyl indole and di acetyl-indole

Anhydrede C₁₈H₁₈N₂O₂ se CH C CO N N_CO C CH C,H, [812°_815°] Mcl

Confirmed by Raoult's methou (Magnani 11, B. 22, 2508) Formed by boiling the acid with

Ac.O using an inverted condenser. Yellow needles

Methyl ether MeA' [152°] Needles Indole (β) -carboxylic acid

C₄H₄ C(CO₂H) CH [214°] Formed by fusing (3) methyl indole (skatole) with KOH (Cia mician, Magnanini a Zatti, 3 21, 673, 1929) Obtained also by fusing (8) acetyl indole with caustic potash (Zatti, B 22, 664) Plates (from water), decomposed on fusion Sl sol benzene and boiling water, m sol alcohol and ether, almost insol. ligroïn Its aqueous solution evolves CO, on boiling With isatin and H.SO. it gives a brownish violet colour Its ammonium salt gives pps with CuSO, and with FeCl. It does not yield a picric acid compound.

Indole di carboxylic acid

 $CO_2H C_0H_4 < \stackrel{CH}{\sim} CCO_2H$ [above 250°] C^{\bullet_4} tained by saponifying its acid ether, which is formed when CO Et C, H, N, H CMe CO, Et, the product of the condensation of hydrazido benz one ether with pyruvic ether, is heated with zinc dust (Roder, A 236, 169) Slender needles, sol. hot alcohol and acetic acid, al sol ether and water Does not colour pine wood Decomposed on fusion giving off CO2 and yielding a product that behaves like indole towards pine wood.

Mono ethyl ether LtHA" [250°] Yellow

needles (from HOAc) INDOLES Alkylated derivatives of indole may be formed synthetically in the following ways (a) By removal of NH, from the phenyl hydrazides of ketones, aldehydes, or ketonic acids Thus with the phenyl hydrazide of acetone C_4H_5 \₂H CMe = NH₃ + C_6H_4 < $\frac{CH}{NH}$ >CMe, in like manner from the phenyl methyl hydra zide of pyruyic acid C,H,N.Me CMe CO;H = NH₂+C₆H, CH_{Me} C CO₂H (E Fischer, A 236, 116) (b) By elimination of NH, from alkylated dı pyrroles -

(Dennstedt, B 21, 3429) (c) By heating (8) bromo & acetyl propionic acid with aromatic amines (Wolff, B 21, 3360) Thus o- or ptoluidine gives tri methyl indole, (8) naphthylamine gives di methyl (8) naphthindole, while ethyl aniline forms di methyl ethyl-indole.

C.H., NHEt + CH., CO CHBr CH...CO.H

= $HBr + H_2O + CO_2 + C_6H_4 < \frac{CMe}{NEt} > CMe$ Indoles may be converted by alkyl iodides into derivatives of quinoline dihydride

CH CMe

CH SMeI = CH CH

NMe CH +3HI

INDOLINE v Indigo INDONAPHTHENE The hypothetical hydrocarbon C,H, or C,H, CH >CH which stands in the same relation to indole that naphthalene stands to quinoline (Baeyer a. Perkin, jun, B 17, 122) The name undere has also been proposed for thesamehydrocarbon (Roser, A 247, 132), v also METHYL INDONAPHTHENE Besides the methods mentioned below, indonaphthene derivatives may be formed by condensation of naphthalene de

CO CO CHCl CCl₂ Thus C.H.

the chlorination of (B)-naphthoquinone is con-

C(OH) CO₂H NaOH into CCl₂ (Zincke, B 20, 2894) which

may be oxidised by chromic acid to

 $C_{\bullet}H_{\bullet} < \stackrel{CO}{cHCl} > CCl_{2}$ [59°]

INDONAPHTHENE DIHYDRIDE CAR BOXYLIC ACID C10H10O2 16

 $C_{\bullet}H_{\bullet} < CH_{\circ} > CH CO_{\circ}H$ Hydrindonaphthene

Formation —1 By heating the correspond ing di carboxylic acid until the evolution of CO2 has ceased, and distilling the product (Baeyer a Perkin, jun, B 17, 122)—2 By the action of (1 mol of) ω -di bromo xylene (o xylylene bromide) upon aceto acetic ether (1 mol) and NaOEt (2 mols) and saponification of the product with alco holic KOH (Scherks, B 18, 378)

Properties - Colourless needles (from water). may be distilled when quickly heated Sl sol cold water On oxidation with KMnO, it yields phenyl-glyoxylic acid It forms a bulky white

silver salt, si sol hot water

Indonaphthene dihydride dicarboxylic acid C₆H₄<CH₂>C(CO₂H)₂ [199°] Formed by the action of di w bromo o xylene on malonic ether (1 mol)and NaOEt (2 mols) in ether (Baeyer a Per kın, jun, B 17, 122, Perkın, jun, C J 53, 7), the resulting ether being saponified Trimetric plates, m sol hot water, alcohol, and ether, sl sol cold water When heated above 200° it gives off CO_2 and leaves the mono carboxylic acid $-Ag_2A''$ white amorphous pp becoming white amorphous pp becoming orystalline, sl sol water INDONAPHTHOQUINONE C,H,O,: 6

 $C_0H_4<_{CO}^{CO}>CH_2$ [131°] Di keto indonaphthene Di keto hydrindene Formed by warming its carboxylic ether C₆H₄<CO>CH CO₂Et with alkalıs (Wislicenus, A 246, 351) Best obtained by acidifying an aqueous solution of the sodium derivative C6H4 C2O2 CNa CO2Et, extracting with ether, and leaving the ethereal solution to stand, when CO₂ is given off

Properties - Small needles (from benzene ligroin), v sol hot alcohol and benzene, m sol ether and hot ligroin, v sl sol cold ligroin and Dissolves in alkalis with intense yellow water colour

Reactions -1 Gives a phenyl hydrazide C_eH₄CO CH₂ [163°] crystallising in yellow needles, insol water and ligroin, v e sol ether and benzene With phenyl hydrazine at 100° it gives rise to a di phenyl hydrazide C.H. C(N,HPh) CH2, which forms coloured plates [171°], and when dissolved in HaSO, is coloured deep bluish green by FeCl, (W

Wislicen 252, 73) -2 Forms a a Kötzle, nitroso erivative C.H. COC NOH [198°] crystalliung from HOAc in triangular plates -8 Be work aldehyde at 120° forms $C_6H_4 < CO > C$ CHPh [150°] -4 Gives with bromine a compound C,H, CC > CBr, [177°] crystallising in plates, m scl hot alcohol and HOAc, v sol ether and C32 (cf Zincke, B 20, 3216) This di bromo derivative, which is also formed by the bromine on C₆H₄ CC — CNH₂ CNH₁ - CNH₂ and on C_eH , CO — C NH_2 , is converted by the action C(NH) CHof alkali into bromoform, phthalic acid, and the compound C₆H₄<COH CBr [118°], whence Br forms again the original CaH CO CBr. while Cl forms C4H4CO>CClBr [147°] (Zincke, B 21, 2394) The corresponding C_sH_s CO CCl₂ [125°] is formed by the action of chlorine on C_oH, CO CO CO COl₂ CCl₂ CCl₂ CCl₃ CCl₄ CCl₅ dissolved in

Indonaphthoquinone carboxylic ether C₆H₄ CO CH CO Et [78] Formed by the action of NaOEt (2 mols) on phthalic ether (1 mol) and subsequent treatment with acetic ether, the product C,H, CO CNa CO F1 being treated with dilute H SO, (Wislicenus, A 246, 349) Slender yellow needles, insol water, v e sol alcohol, ether, benzene, and ligroin FeCl, colours its alcoholic solution deep red Dissolves in aqueous Na₂CO₃, expelling CO If its alkaline solution be boiled and then acid: fied CO2 is evolved and indonaphthoquinone libe rated It forms a phenyl hydrazide If its acid solution is boiled with water there is formed C18H10O3, which dyes wool violet red and forms orystalline C18H2BrO, [196°] and C18H2Br2O, $[242^{\circ}]$

aqueous Na₂CO,

Salts -C,2H,O,Na aq yellow needles (from Gives with Mel the compound CoH. CO>CMe CO2Et, orystallising in prisms [74°], v e sol alcohol and ether, insol water, sol NaOHAq with rose colour - (C12H,O), Cu green crystals (from alcohol)

INDONE The ketone CaH, CO>CH, a number of the haloid derivatives c* which have been described by Roser (A 247, 132) Indone may also be viewed as the anhydride of DI oxy INDOMAPHTHENE

INDOPHANE C₂₂H₁₀N₄O₄. A blue substance, resembling indigo, produced, together with naphayl purpure acid, by adding a hot concentrated solution of KCy (45 g) to limitro naphthol (f') g) dissoived in boiling water (2 litres) to which just enough NH, has been added to effect

INDOXYL 7

solution (Hlasiwetz, Sommaruga, C C 1871, 617) Violet mass with green lus' , insol. water, alcohol, ether, benzene, and C., m sol H₂SO₄ and hot HOAc, forming purple solu-tions Ma be sublimed Nitr c acid converts it into a brownish red body, soluble in alkalis Ferrous sulphate mixed with lime reduces it Aqueous KOH forms C₂₂H₂KN₄O₄aq, a body greatly resem ling indigo, NaOH acts in like manner

INDOPHEFAN (C,2H,NOS)x Formed by shaking isatin (1 pt) with H2SO, and benzene that contains thiophene C₈H,NO₂+C₄H,S=H₂O+C₁₁H,NOS (Baever, B 12, 1309, 16, 2188, 18, 2637, V Meyer, B 15, 2893, 16, 1465, P Meyer, B 16, 2269, Gumpert, J pr [2] 32, 278) Blue powder, which exhibits a coppery lustre when rabbed, or small needles (from alcohal phenol) Insol water, benzene, and ligroin, v si sol alcohol, ether, and CS₂, si sol HOAc in H₂SO₄ it forms a blue solution, whence it is ppd by water Cannot be sublimed May be re duced by zinc dust and HOAc to a colourless body which is re oxidised to indophenin on ex pos ire to air Bromo, di bromo, and methyl indophenins may be formed in like manner by using bromo, di bromo, or methyl isatin in place of isatin in the above preparation

INDOPHENOLS Quinonimides of the formula $C_eH_i <_{NR'}^{NH}>$, where R' is an aromatic radicle containing hydroxyl (of Indamines). Thus when a mixture of di methyl p phenylene diamine and (a) naphthol is oxidised with NaOCl or K2Cr2O there is formed the dark blue indophenol

NMe₂Cl (Pabst, Bl [2] 38, 161), C₁₀H₄ OH (Pabst, Bl [2] 38, 161), while p amido phenyl piperidine mixed with phenol and oxidised by K, FeCy, forms a similar

body C,H,CI (Lellmann a Geller, B

21, 2288)

INDOTANTHIC ETHER $C_{ii}H_{ii} \times O_4$ se. C,H,<CO>C(OH) CO,Et [107] Prepared

by the careful exidation of indexylic ether with $1 \, e_i \text{cl}_{\bullet}$ (Baeyer, B 15, 775) Yellow needles or monoclinic prisms Sol water needles or monoclinic prisms and ether On further oxidation it gives CO H C, H, NH CO CO, Et On reduction it is recorverted into indoxylic ether Decomposed by alkalis with formation of anthranilic acid

Nitrosamine C11H10(NO)NO4 [113°] Light yellow needles or tables Sol alcohol and

ether, sl sol water

Indoxyl $C_{\bullet}H$, no 1 e $C_{\bullet}H$, $< C_{NH}^{C(OH)} > CH$ (stable form) or C₆H₄ CO CH₂ (transition (orm)

Formation -1 By warming potassium in doxyl sulphate with HCl or H SO, -2 By heat ing indoxylic acid alone or with H.SO, (Bacyer, B 14, 1744) -3 By boiling o nitro phenyl ace tylene with acid ammonium sulphite, and tree t ing the product with zinc dust and ammonia (Baeyer, B 15, 56) -4 By reducing isatogensulphurous soid with zinc dust and ammonia

Properties —Oil Not volatile with steam. In the pseudo form C₈H₄ CO_{NH} CH₂ it is not knowr in the free state, but di substitution products of \(\psi \) indoxyl are stable. Nevertheless in doxyl forms condensation products, called in dogenides, with bodies containing a CJ group, in which reactions it must be supposed first to change into the pseudo form

Reactions -1 In alkaline solution it is rapidly oxidised in the air to indigo FeCl, forms a white amorphous body, which is imme diately converted by HCl into indigo (E Bau mann a Tiemann, B 13, 415) -2 Indoxyl is not affected by H_2SO_4 or cone HClAq, but dilute HClAq converts it into an amorphous red sub stance -3 A solution in H2SO, treated with o nitro-phenyl propiolic acid gives indoin -4 On warming with a solution of Na₂CO, and o nitrophenyl propiolic acid, indigo is produced -5 By the action of Na₂CO₂ upon an alcoholic solu tion of isatin and indoxyl there is formed indi rubin, while with bromo isatin the product is bromo indirubin (Baeyer) — 6 Bromine gives tri bromo aniline (E. Baumann a Tiemann, B12, 1192) -7 In alkaline solution K,S,O, forms indoxyl sulphuric acid -8 Diazo benzene chlor 1de forms C.H. COH, N.Ph CH? [236°] (Baeyer,

B 16,2190)

Nitrosamine C.H. COH, SCH Formed by the action of nitrous acid on indoxyl (Baeyer, B 16, 2188) Slender yellowish needles When boiled with HCl it gives indigo

Isonitroso derivative of \(\psi \) indoxyl

 $C_{\bullet}H_{\bullet} < CO > C \text{ NOH}$ See oxim of ψ isating

Ethyl derivative C.H. COEt) CH.

Tormed by heating the ethyl derivative of in doxylic acid Oil, volatile with steam Smells like indole, and colours pine wood, acidified with HCl, brownish red Its pierie acid com pound C10H11NOC, H2(NO2), OH forms brown needles Its nitroso derivative

C.H. $\langle \stackrel{C(OL,t)}{\sim} \rangle$ CH forms yellow prisms [85°], sol alcohol, insol water, and converted into indigo by heating with HCl (Baever, B 15, 781)

Indoxyl sulphuric acid C.H NSO. in the urine of herbivora and, in smaller quan tity, in that of man (Schunck, P M [4] 14, 288, Hoppe Seyler, C C 1864, 511, H 8, 79, E Baumann a Tiemann, B 13, 408) When in dole is introduced into a dog by injection or in food large quantities of indoxyl sulphuric acid appear in the urine (Jaffé, Fr 11, 358, E Baumann a Brieger, H 3, 254) Indoxyl sul phuric acid is also formed by adding K,S,O, to a solution of indoxyl in aqueous KOH (Baeyer, B 14, 1745)

Potassium salt -KA' Plates (from hot alcohol) V sol water, v sl. sol cold alcohol Not affected by KOH even at 170° Decomposed by hot dilute HCl or H₂SO,, or even by water at 120°, into indoxyl and I TSO, When warmed with FeCl, and a little HCl it is entirely converted into indigo Indigo is also formed when the salt is heated alone.

INDONYLIG ACID C,H,NO, re

C,H, C(OH) O CO,H (stable form) or

CO

C_cH_cCO_{NH} CH CO₂H (transition form) [123°]. Formed by saponifying its ether with fused NaOH at 180° White crystalline pp, sl sol water. In dilute alkaline solutions it is converted into indigo by the action of air or oxidising agents. On heating it splits off CO₂ forming indoxyl

Indoxylic ether C₈H₅N(OH) CO₂Et Colourless prisms, [121°], dissolves in alkalis and is reppd by CO₂ Prepared by reduction of isatogenic ether or o nitro phenyl propiolicether Heated with H₂SO₄ it gives indigo sulphonic soid On oxidation it gives successively indo xanthydic ether C₂,H₂₀N₂O₃, indoxanthic ether C₁₁H₁₁NO₄, and hydrogen ethyl oxaloxyl o amido benzoate CO₂Et CO NH C₈H₄CO₂H

Acetyl indoxylic ether
C.H.N(OAc) CO.Et white needles, [138°]
Ethyl indoxylic ether

C_aH_aN(OEt) CO_cEt large colourless crystals, [98°]

Ethyl-indoxylic acid C₂H₄N(OEt) CO₂H plates, [160°] Oxidised to indigo by Fe₂Cl₈, but not in alkaline solution

Nitroso-ethyl-indoxylic acid C₈H₄N(NO)(OEt) CO₂H flat golden needles Decomposes at about 200° Formed by the action of nitrous acid on ethyl indoxylic acid (Baeyer, B 14, 1742, 15, 775, 16, 2189, Forrer, B 17, 376)

INDUCTION When H and Cl are mixed in equal volumes and exposed to sunlight a measur able time elapses before chemical change begins Bunsen a Roscoe, who examined this phenome non (T 1857 355), regarded the mixture as resisting chemical change, and they used the term induction to express the gradual overcoming of this resistance. The term has also been used by Wright, who noticed a similar phenome non in the reduction of metallic oxides by CO and H (C J Trans 1879 475, 1880 757), Chemical Change, vol 1 p 749

MMPM INDULINES (O N Witt a Thomas, C 43, 112) Coloured compounds formed by the action of such bodies as azo, amido azo, nitro, or nitroso- compounds on the hydrochlorides of certain aromatic amines with elimination Anılıne hydrochloride gives a darkof NH, blue colouration with amido azo benzene mann a Geyger (B 5, 474) supposed that only one dye stuff was formed $C_{12}H_{11}N_3 + C_6H_1N$ = C₁₈H₁₅N₂ + NH₃ In reality a great number of dye-stuffs are got If the mixture of diazo benz ene anilide (1 pt), aniline (4 pts), and aniline hydrochloride (1 pt), which has been left until the diazo benzene anilide has changed into amido azo-benzene, be heated at 100° for 24 hours, crystals of azophenine C₁₀H₂₁N₄ separate This forms garnet coloured leaflets (from aniline) [237°] (v Azophenine) If the mixture of aniline, aniline hydrochloride, and amido azo-benz-ene, after heating at 100° till azophenine is formed, be further 1 sated at 125°-180° for 12 hours, the azophenine disappears, and the mass turns blue If it be slowly cooled crystals are These may be separated from the

mother-liquor (which contains 'induline B'), washed "th spirit and wi'h boiling water, and recrystal sed from aniline mixed with aniline hydrochloride So obtained, induline 3 B forms glistening brown leaflets, C₂₀H₂₂N₂ECl It is insol cold, sc' hot, spirit, and v sol aniline Alcoholic NaOH liberates the free base, which forms purple solutions with alcohol and with aniline Induline 3 B is sky blue Its sulphonic acid resembles that of induline B

Induline 6 B—C_{3e}H, N₅ Is formed by heat ing a mixture of amido azo benzene (100 pts), aniline hydrochloride (130 pts), and anil ne (300 pts), for 5 hours at 110°, then adding more aniline hydrochloride (65 pts), and heating to 165°–170° The hydrochloride, B'HCl, separates as green crystals The iree base separates from aniline as brilliant green needles. The solution of this base is of a dark bluish purple colour The hydrochloride is insoluble in the usual solvents, and is hardly soluble in aniline. It dissolves in phenol and in H₂SO₄, forming a greenish blue solution

Induline B hydrochloride is v sol spirit, sl sol water, v sol a cone aqueous olu tion of aniline hydrochloride. The base forms a brown red spirit solution. The sulphonic acid is insol water, but its neutral alkaline salts form reddish blue aqueous solutions.

Formation of indulines is due to the dehy drogenating action of amido azo benzene, which itself becomes aniline and p phenylene diamine, the latter then entering into the reaction A/o benzene, phenyl amido azo benzene, chrysoid ine, nitroso di methyl aniline, and even amido azo naphthalene, may be substituted for amido azo benzene, but if instead of amiline o toluidine or naphthylamine be used, red dyes are got (azo toline, &c) This would indicate that azophen ine was an oxidation product of aniline, and not derived from the amido azo benzene. In the preparation of azophenine by heating aniline (4 pts) with aniline hydrochloride (1 pt) and amido azo benzene (2 pts) at 85, am monium chloride and p phenylene diamine are constant by products, indicating that phenyla tion and reduction of the amido azo benzene has taken place (Witt, B 20, 1539) When azo phenine (400 g) is boiled with alcohol (40 litres) and strong H2SO4 (2 kilos) for 10 hours quinone dianilide (195 g) is formed The compound C_dH₄ NPh is converted by heating with ani line at 100° into azophenine (Baudrows' i, M These reactions confirm the formula 9, 414)

C₈H₂(NPhH)₂ | Proposed by Kimich and by

Fischer a. Hepp for azophenine, which is also consistent with its formation from nitroso di-N---HPh

phenylamine C.H. NHPh (O Fischera Hepp,

B 20, 2479, 21, 676, 2617) By the action of aniline on azophenine, induline (6 B) of the formula NPh C₄H(NHPh)₄ NPh C₄H, might be formed A mixture of 8 B and 6 B induline is

formed A mixture of 8 B and 6 B induline is formed by heating p-nitroso di-phenyl amine with aniline and aniline hydrochloride in alcohonic solution at 130° By heating p nitroso-di-

INOSITE 9

phenyl amine (1 pt) with aniline hydrichloride (1 to 2 pts) and ar 'ine (4 pts) at '5°-140°, a very rich yield of induline is obtained, which chiefly consists of 6B. If pure azophenine is heated at 140° with equal parti of aniline and aniline hydrochloride 6B induline is almost exclusively formed (Fischer a Hepp, B 20, 2484). By the action of azo, intro, or mitroso compounds on m-or p-dirmines, indulines which are soluble in water are formed, e.g. paraphenylene blue.

Rosinduline C28H19N, te

C_{1e}H₃(NPn) $\stackrel{N}{\sim}$ N_{Ph} $\stackrel{N}{\sim}$ C₆H₄ [225°] Formed by the action of nitroso phenyl (a)-naphthylamine hydrochloride on aniline and aniline hydrochloride at 120° (O Fischer, B 21, 2621) Formed also by oxi ising triphenyl tri amido-naphthelene C_{1e}H₃(NHPh), [1 2 4] Red plates, almost insol water, m sol alcohol, v sol benzere Reduced by HI and P at 150° to a yellowish red base and aniline Zinc and HCl give naphthalene and aniline

Salts ¬B'HCl 1 aq reddish brown prisms
—b H PtCl₆ —B'H₂SO₄ aq B'HNO₄ [231°] —

Picrate plates, insol water INDYL PHENYL KETONE CARBOXYLIC

acid C_sH_s CO C_sH_s CH_s CO.H Benzo endok carboxylic acid [285°] From the eso benzo₁ phenyl hydrazide of tyruvic acid by heating with ZnCl, at 220° (Ruhemann a Black man C J 55, 617) White needles, at sol. boiling water Decomposes on fusion

INOGEN v MUSCLE

INOSIC ACID $O_{10}H_{11}N_1O_{11}$? Occurs in the mother liquor in the preparation of creatine from flesh (Liebig, A, 62, 317, A, Ch, [3, 33, 129) Occurs to the extent of $\frac{1}{4}$, pc in the flesh of hens. Pigeon's flesh and human flesh contains none (Gregory, A, 64, 106, Schlossberger A, 66, 82). It is found in some fish (Limpricht, A, 133, 301)

Preparation - The filtrate from which creatin has separated is concentrated, then mixed with alcohol till it acquires a milky consistence, and left to itself for a few days. It then deposits a crystalline mixture containing the inosates of Na and Ba. The crystals are dissolved in hot water and BaCl, added. The Ba salt crystallises on cooling.

Properties —Uncrystallisable, v sol water, forming a solution with a flavour of broth, whence alcohol ppts it as an amorphous powder Insolution

Salts - K,A" 7 aq long, four sided prisms, ▼ sol water insol alcohol - BaA" 6 aq prisms 8 25 at 16°

INOSITE C.H. O. Phaseomannte [217°] (Maquenne), [225° cor] [Fick) (319° in vacuo) (M) SG (of C.H.,O.,2aq) L2 1524 SG (of C.H.,O.,2aq) L3 1524 SG (of C.H.,O.,2aq) L3 1525 SG (of C.H.,O.,2aq) 10 at 12 (T a V), 13 at 19° (Fick) H C 666500 H F 311500 (Berthelot a Recoura, C R 105, 14° Discovered by Scherer (A 73 322, 81, 375) in muscular substance (Is, ivos, muscie) It occurs especially in the heart, but also in the lungs, kidneys, liver, and spleen of oxen (Cloetta, 199, 289) in the train of oxen (W Millex, A 103, 140), in human kidneys, and in the urine in a case of Bright's disease to the amount of 1 p c.

and sometimes in healthy urine (Kulz, Fr 16, Found also in birds, in cephalopoda (Krukenberg, J Th 1881, 343), and in the flesh of a young porpoise (O Jacobsen, A 157, 227) Inosite occurs in green kidney beans (Phaseolus vulgaris) (Vohl, A 99, 125, 105, 330), in the green nods and unripe seeds of peas (Pisum sativum). in unripe lentils (Ervum Lens), in the unripe fruits of the common acacia (Robinia Pseud-Acacia), in the heads of the common cabbage (Brassica oleracea, var capitata), in foxglove leaves, in extract of digitalis, in the leaves of the dandelion (Taraxacum dens leonis), in potato shoots, in green asparagus and in its berries, in Lactaria piperatus, in Claiaria crocea (Marmé, 4 129, 222), in the leaves of the common ash (Frazinus excelsior) (Gintl, J pr 104, 491), in grape juice (Hilger, A 160, 333), in young vine leaves (Neubauer, Fr 12, 45), in walnut leaves (Tanret a Villiers, A Ch [5] 23, 389, C R 86 486, Maquenne, C R 104, 225)

Preparation -1 Walnut leaves are extracted with water The brown liquid is treated, at 100° with excess of milk of lime, filtered, ppd with lead acetate, again filtered and treated with am monia and lead acetate The crude lead com pound of mosite is treated with dilute sulphuric acid, and the mosite is ppd with alcohol and other It can be further purified by recrystallisa tion from hot dilute acetic acid (Hilger, Ma quenne) -2 The fresh-chopped tissue is covered with water, and allowed to stand for 24 hours in a cool place with frequent stirring, the liquid is then separated and the residue pressed, the solution is heated with a little acetic acid to separate albumin and hæmatin, then strained, evaporated on the water bath to one tenth, ppd with neutral accetate of lead and filtered, and the filtrate is mixed with basic acetate of lead, whereupon mosite is thrown down in combina tion with oxide of lead, accompanied by urio acid, evstine, and other substances The pp, after washing, is decomposed under water by H S, and the liquid filtered from the sulphide of lead, it then sometimes deposits crystals of urio acid, and when evaporated to a small bulk on the water bath, and mixed with alcohol till a tur bidity is produced, it yields crystals of inosite (Cloetta) -3 Crystals of mosite may often be obtained by evaporating an aqueous liquid containing it, and adding three volumes of alcohol to one of the boiling liquid (Cooper Lane, & 117

Propertu . - Monoclinic crystals (containing 2aq) $a \ b \ c = 1\ 090$ 1 1 5 35, $\beta = 111^{\circ} \ 39'$ Effloresces in dry air At 100° it gives off its water of crystallisation It has a sweet taste and is optically mactive Sl sol cold dilute alcohol, insol absolute alcohol and ether Does not combine with NaCl or kCl With lead sub acetate it forms a gelatinous pp which may be C, H, O, 2PbO Inosite does not react with phenyl hydrazine (E. Fischer, B. 17, 582) Ino. site is not turned brown by boiling alkalis, or by boiling dilute H.SO. It does not reduce Feh ling's solution but forms a green pp It will not undergo alcoholic fermentation In presence of decaying cheese or of putial meat and chalk it forms butyric and lactic acids Sodium amalgam does not affect mosite Inosite does not form an acid solution with borax

10 INOSITE.

Reactions -1 Evaporated with nitric acid it leaves a residue which gives with CaCl, in ammoniacal solution a rose red colouration (colour test) -2 When a solution of in osite is evaporated nearly to dryness and a drop of mer curic nitrate solution is added there is formed a yellow pp which turns red on warming (Galloir, Fr 4, 264) —3 Heated with oxalic acid it gives CO, and formic acid According to Lorin (Bl [2] 48, 235), this indicates that it is a polyhydric alcohol -4 HIAq at 170° gives a trace of benzene, phenol, and tri iodo phenol [153°] -5 It forms no addition products with chlorine and bromine -6 It does not reduce boiling ammoniacal AgNO, but on adding KOH a mirror is formed -7 Chromic acid oxidises it to CO, and formic acid in the cold —8 KMnO, gives CO, — 8 Conc HNO, at 100° forms oxalic acid, but in an open dish on the water bath it gives on eva poration a white substance which dissolves in water, and the solution, mixed with alcohol and evaporated, then deposits black crystals of tetra oxy quinone HNO, also forms rhodozonic acid (Maquenne, Bl [2] 47, 290) According to Maquenne this reaction, and reaction 4 indicate that mosite is hexa oxy benzene hexahydride

Hexa-acetyl derivative C. H. (OAc). [212°] (234° invacuo) From mosite and AcCl or Ac,O Sublimes at 200° Insol water, sol hot alcohol and Ac,O Saponified by alkalis and strong acids (Maquenne, C R 104, 1719, Bl [2] 48, 58) According to Fick (C C 1887, 452), the acetyl derivative is C. H. Ac,O. and

melts at 216 cor

Hexa-benzoyl derivative $C_sH_o(OBz)_s$ [258°] Minute needles Insol all usual sol vents

Hexa nitroxyl derivative C.H. (ONO), 'Nitro inosite' [120°] Formed by adding a solution of inosite in fuming HNO, to cone H.SO. May be crystallised from alcohol, a crystalline tri-nitroxyl derivative being left in the mother liquor Trimetric tables, insol water, v sol alcohol Detonates when struck Cold alcoholic KOH decomposes it forming KNO, the inosite being completely broken up When boiled with alcohol and a little H.SO. the pro

ducts are nitrous ether and inosite

INULIN (C₈H₁₀C₃), or C₇H₁₄C₉₂ Helenin Alantin Menyanthin Dahlin Synanthin Sinistrin Mol w 1980 (by Raoult's method Brown a Morris, C J 55 464) [160°] S G 1 35 (Kiliani), 1 36 (Payen), 1 46 (Dubrunfaut), 1 47 (Dragendorff) [a]_D = -35° (Dubrunfaut, C R 42, 803), -36 5° (Lescœur a Morelle, C R 57, 216), -40° (Lefranc, J Ph [5] 2, 216) H C 684900 (Berthelot a Vieille, Bl [2] 47, 868, A Ch [6] 10, 459) H F 230600 (B a V), 197000 (Von Rechenberg) A starch like substance occurring in the roots of elecampane (Inula Helenium) (Valentin Rose, A D 1804), dandelion (Taraxacum dens leonis), chicory (Cichorium Intybus), feverlew (Pyrethrum Parthenium), and meadow saffron (Colchicum au tumnale), in the tubers of the potato, the dahlia, affd the Jerusalem artichoke (Helianthus tuberosus), in Lerp manna (from Eucalyptus dumosa), and in ce. and lichens (Luchen frazzeueu and Luchen fastigatus) Sinistin, from the sea onnon (Urginea Scilla), is perhaps identical with inulin

Preparation—The finely divided roots are boiled v h water in pression of a small quantity of C.CO. The filtrate is cooled by a freezing mixture, and, after thawing the ice, filtered again. The up is redissolved in hot water, and the filtred solution again subjected to the action of a freezing mixture, the process being repeated until the inulin is perfectly white. The inulin is then freed from traces of levulose by treatment with 97 p c alcohol, and is finally dried over sulphuric acid. It will, however, contains about 6 pc proteid matter corresponding to 1 pc nitrogen, and also minute traces of in orga is substances (Kiliani, A. 205, 147)

Properties - White powder, resembling starch Tasteless Occurs also in a gum like or horny modification, probably as a hydrate SI sol cold water, v sol hot wa er, insol alco hol The powder is composed of minute sphere-(Sachsse) It melts at 160°, becoming changed to amorphous 'pyro inulin' (Prantl, N R 19, 513, 577, 641) Inulin is very hygroscopic, and even when dried at 100° its composition appears to be (C₄H₁₀O₅)₄H O (Kiliani) The aqueous solution of inulin does not form a jelly like that of starch It is not coloured blue by It dissolves in cold aqueous KOH and iodine the solution, when acidified, deposits after a while unaltered inulin It dissolves in am moniacal cupric oxide solution (Cramer, J pr 73, 16) the sol tion yielding after a few hours a copious blue pp (Schlossberger, J pr 73, 373) It dissolves in an ammoniacal solution of nickel oxide It does not ppt lead acetate or sub acetate, but with a solution of lead acetate con taining ammonia it gives a white pp Inulin is not ppd by salts of Fe, Cu, Hg Ag, or Au Inulin forms with alkalis unstable compounds which are soluble in water and ppd there from by alcohol When carbonised it emits an odour of burnt sugar It reduces ammoniacal gold and silver solutions, but not Fehling s solution It is not fermentable, nor is its optic activity affected by diastase It is not converted into levulose by invertin A solution of inulin dissolves PbO Baryta water gives a pp soluble in excess of a solution of inulin, and not decom posed by CO,

Reactions -1 When heated with water at 100° it is slowly but completely converted into levulose -2 Boiling dilute acids quickly con vert it into levulose - 3 Dilute nitric acid oxi dises it to racemic, oxalic, glycollic, and formic acids, but forms neither saccharic nor muc c acids (Tollens, A 249, 220) -4 By long contact with bromine it yields bromoform, oxalic acid, and CO2 -5 With bromine and silver oxide it yields glycollic acid (from the intermediate formation of levulose) -6 When heated with baryta water small quantities of lactic acid are formed -7 Sodium-amalgam has no action on inulin-8 With chloro sulphuric acid (CISO,H) at 0° it forms $C_0H_7(SO_4\tilde{H})_4(O)Cl([a]_D = +11\frac{10}{2})$ whence warm water produces levulose (Claesson, J pr

128, 27)

Acetyl delivatives Inese are best formulated as derivatives of $C_{12}H_{29}O_{10}$

Trs-acetyl derivative C₁₂H₁,Ac₂O₁₀ Formed by boiling mulin (1 pt) with Ac₂O₁O₁ pt and HOAo (2 pts) for 15 minutes (Ferroullat a Savigny, Z. [2] 5, 509, Lescour a Morelle, OR 87, 216) Amorphour yellowish me 1, v sol water and alcohol, ir ol ether Lawo _atory

Tetra acetyl derivative C, L, L, Ao, O, From inulin by heating with A, O (F a S, Schützenberger, A Ch [4] 21, 234 Amorphous Leworotatory

Hexa acetyl derivative C₁₂H₁₄Ac₆O₁₆ Amorphous Lævorotatory

Hepta acetyl derivative C12H13Ac,O10.

Dextrorotatory

When inulin is heated with gly Metinulin cerin alone, or when it is heated with dilute acids, the product contains bodies resembling dextrin. They are not very soluble in ater and on heating yield soluble metinulin and inuloid which are not so powerfully laworota tory as the unaltered inulin Optically inactive derivatives are also formed, but they are not id ntical with levulosan (Hönig a Schubert, M 8, 529) Metinulin was prepared by Dragendoiff by heating inulin (1 pt) with water (5 pts) in a Inuloid is closed vessel, and ppg with alcohol a similar or identical substance, said by Popp (A 156, 197) to occur in the Jerusalem arti It is twice as soluble in water as inulin choke

INVERTING FERMINATION, vol. in p. 541

IOD or IODO Use of this prefix applied to inorganic compounds and Iodo salts v the element the iodo compound of which is sought for or the salts to the name of which iodo is prefixed. Thus we childred of lead will be found under Li up and iodo chromate of potassium under Chromates.

10DATES and PERIODATES Salts of vodic and periodic acids v Iodine, Or acids of, pp 21, 23

IODATION v IODO COMPOUNDS

(Strecker, W 17, 447)
$$\frac{5 \text{ Hp}}{5 \text{ H} \text{ V}}$$
 (20°) 1397,

(100°) 1396 (Stiecker, lc) 1 (of HIAq v hohlrausch, P 159, 233 SG of HIAq st trated at 0°-199 (De Luynes A Ch [4] 2, 3s-1), 20 (Vigier, Bl [2] 11, 125) Vapour pressure of liquid HI at -17 8° -2 9 atmos, at 0 = 4 atmos, at 15 5°=58 atmos (laraday, T 1845 170, values approx only) HF [H, I] = -60 36° gaseous H and solid I to form gaseous H1, [H, I] = -436 gaseous elements at 1s0, [H, I, Aq] =13,170 (Th 2, 35) HI does not occur in nature

Formation – 1 By direct union of H and I, by passing a stream of H over I at a full red heat (Courtois, A l'h 88, 305, Merz a Holzmann, B 22, 869) Corenwinder passes H and I tunnel, and a single drop of this is allowed to vapour over Pt black heated to 300°-400° (A Ch [3] 30, 242, 34, 77, v also Blundell, P 2, 216, Lemoine, C R 85, 34) —2 HI is formed by decomposing a metallic iodide by another acid, but a portion of the HI is generally decomposed with separation of I, and in some cases the HI reacts with the other acid, cg when H₂SO₄ is added to kI, SO₂ and H₂S are produced as well as HI and I. To prepare a solution of HI 17 water, Glover adds as exactly equivalent quantity of H₂SO₄ to BaI₂Aq, and separates from ppd BaSO₄ (P M [3] 19, 92)—

Hold into the tubulus of the retort, 5 g amolphous P and 10 g water are placed in the funnel, and a single drop of this is allowed to flow into the retort, after a little a drop or two more is allowed to follow, and a little later the flund is added in larger quantities. HI passes off and may be collected in water as described under 1. No heating is required If more than one drop of the P in water is added at first an explosion usually follows. The I carried over is nearly all deposited on the neck of the retort, 5 g amolphous P and 10 g water are placed in the funnel, and a single drop of this is allowed to flow into the retort, after a little a drop or two more is allowed to follow, and a little later the flunds is added in larger quantities. HI passes off and may be collected in water is added at first an explosion usually follows. The I carried over is nearly all deposited on the neck of the retort, 5 g.

1 to 1 the funnel, and 10 g water are placed in the funnel, and 10 g water are placed in the funnel, and 10 g it for interesting the funnel, and 10 g water are placed in the funnel, and 10 given the funnel

3 By the reaction between Na₂SO₂ (Mène, C R 28, 478), or Na₂S₂O₂ (Gladstone, P M [3] 35, 345), I, and H₂O (cf formation of HBr, vol 1 p 532) -4 By decomposing PI, by water (Kolbs, J pr 15, 172, Vigier, Bl [2] 11, 125, Petten kofer, A 138, 57) Rieckher (C C 1863 207) r commends to make PI, by adding P ω I in CS₂ and distilling off the CS₂ -5 Etard a Moissan (B 13, 1862) heat I with colophony Preparation -1 Washed H₂S is passed into

water in which a little finely powdered I is suspended (2H,SAq+2L,Aq=4HIAq+2S), more I is added little by little, and the passage of H.S is continued. When all the I has been added, and no brown colour is produced on shaking the liquid, the separated S is agglomerated by briskly agitating the vessel, the liquid is filtered, H2S is removed by gently warming, and the liquid is distilled, HIAq of SG c 17 distils at 120°-128° An inverted untubulated retort with wide neck is a suitable vessel, the H2S is passed down the neck of the retort by a tube dipping into the water in which the I is suspended. The HIAq thus prepared may be used for making gaseous HI or a more conc solution About 2 pts I are dissolved in the HIAq made as described, and the solution is dropped from a tap funnel on to amorphous P (in a flask) moistened with HIAq of the same concentration, the HI produced is passed through a wide U tube containing glass beads and some amor phous P moistened with HIAq (to convert any I vapour into HI) [PI, + 3H,O + Aq = H,PO,Aq + 3HI] If dry HI is wished for, the gas is passed through a CaCl, (or better Cal, tube and then over P,O, and collected by downward displacement If HIAq is to be pre pared, the gas coming from the first U tube is passed into the tubulus of a retort, the neck of which dips a very little way beneath the surface of water kept cold by ice this arrangement prevents the water from rushing back into the U tube The flask containing P in HIAq, into which the solution of I is dropped, should be only very gently warmed for some time, as H PO, is among the first products of the reaction, and when this is heated H,PO, and PH, are formed, the latter of which combines with HI to form PH,I to Bannow, B 6, 1498) -2 L Meyer recommends the following method of preparing HIAq by the formation and decom position by water of PI, (B 20, 3381) 100 gI in a retort, with the neck inclined upwards, are moistened with c 10 g water, a tap funnel (or a funnel into the neck of which its a glass rod) is titted into the tubulus of the retort, 5 g amorphous P and 10 g water are placed in the funnel, and a single drop of this is allowed to flow into the retort, after a little a drop or two more is allowed to follow, and a little later the liquid is added in larger quantities. HI passes off and may be collected in water as described under 1 No heating is required If more than one drop of the P in water is added at first an explosion usually follows The I carried over is nearly all deposited on the neck of the retort 8 14 pts KI are warmed with 20 pts I and 1 to 11 pts P with a little rater (Millon, J Ph 28, 99, Roscoe, C J 13, 140) — 4 Na₂SO₂ 28, 478, cf Gladstone, P M [3] 35, 345) — 5 60 g of copaiba oil are slightly warmed in a 500 c c retort connected with a reversed condenser, 20 g of I are added little by little, and the temperature is allowed to rise, after a few minutes a regular and steady stream of HI comes off, when this slackens the retort is allowed to cool somewhat, more I added, and heating is recommenced, about 145 g HI may be obtained from 150 g I (Bruylants, B 12, 2059)

obtained from 150 g I (Bruylants, B 12, 2059) S Kemp (P M [8] 7, 444) says that liquid HI may be prepared by placing H persulphide in one limb of a sealed tube and a little I in the other, and gently warming the persulphide, H₂S is evolved and liquefied, and the I dissolves in the liquid H₂S, on then adding a drop of water (this is done by a special arrangement of the tube) HI is produced and liquefied, no details are given as to how the HI is separated from the H₂S

Properties -HI is a colourless, strongly acrid gas, it is incombustible and extinguishes flame Dry HI is unchanged when kept in closed tubes in the dark (Lemoine, J 1877 138) HI is readily liquefied (v ante), liquid HI is colourless (Kemp, P M [3] 7,444, says it is yellowish), at -55° it solidifies to a colourless, ice like mass (Faraday, T 1845 170) Liquid HI is a very bad conductor of electricity (Bleekrode, W 3, 161, Hittorf, W 4, 374) HI is very soluble in water, the solution contains a strong acid, afti nity of HIAq is about the same as that of HClAq (v Affinity, vol 1 p 82) HIAq 18 a colourless, strongly acid, fuming liquid, the solution saturated at 0° has SG 199 to 20, this solution gives off much HI when warmed to 40°-50° When HIAq containing more than c 57 p c HI is distilled, HI is evolved until the SG becomes c 167-170 when the BP becomes approximately constant at 127° (at 774 mm), and the liquid contains 570 pc HI, if the original liquid contains less than 57 pc HI water distils over until the acid of 57 pc is produced, which then distils at 127° almost unchanged (Roscoe, C J 13, 160) By passing dry H through HIAq at 15°-19°, an acid of constant concentration, 603 to 607 p c HI, is obtained, at 100° the constant acid contains 58 2 to 58 5 p c HI (Roscoe, lc) Topsöe gives the following SG and composition of HIAq (B 3, 403, cf Wright, C N 23, 242)

Temp	8.G referred to H _s O at same temp.	Pc HI	Temp	SG referred to H _s O at ame temp	Рс НІ
0			۰		
13 5	1 017	2 29	13	1 413	40 43
,,	1 052	7 02	٠,,	1 451	43 39
99	1 077	10 15	,,	1 487	45 71
13	1 095	12 21	٠,,	1 528	48 22
135	1 102	13 09	13 5	1 542	49 13
,,	1 126	1ŏ 73	13	1 573	50 75
"	1 164	19 97	125	1 603	52 43
138	1 191	22 63	14	1 630	53 93
,,	1 225	25 86	137	1 674	56 15
18 5	1 254	28 41	13	1 696	57 28
,,	1 274	80 20	125	1 703	57 42
13	1 309	83 u7	187	1 706	57 64
99	1 347	36 07	12	1 708	57 74
**	1 382	38 68			

HI is a worbed by charcoal, according to Favre 22,000 ram thermal units are produced for every 128 g ams HI absorbed (A Ch [5] 1, 209)

Reactions -1 HIAq is decomposed by electroly's to HJ), Aq and H (Riche, J 1858 101) 2 HI is slowly decomposed in sunlight, the decomposition proceeds without limit (Lemoine, J 1877 139) When mixed with oxygen and ex posed to sunlight, even v hen the gases are dry, decomposition occurs, and proceeds the more rapidly the greater the mass of O (dry HCl and HBr are not decomposed under the same conditions) (Richardson, C J 51, 801) HIAq is reaaily decomposed wit' separation of I by ex posure to air -3 HI is decomposed by heat to H and I, slowly at 180° quickly a 440° (Hautefeuille, Bl [2] 7, 198), the dissociation of HI has been exhaustively studied by Lemoine (v Dissociation, vol 11 p 400) —4 Heated 1 th oxygen H₂O and I are formed —5 Chlorine forms HCl and I, with excess of Cl, ICl, is produced, bromine leacts similarly -6 Sulphur and selenion form H S, or H Se, and iodide of S or Se (Hautefeuille, Bl [2] 7, 198), in presence of water I reacts with H.S to form HIAq and S (v Preparation No 1) -7 HI is without action on amorphous phosphorus at 100°, but with or dinary phosphorus, even at the ordinary tempe rature, it forms P₂I₄ HIAq slowly reacts with excess of P to produce H,PO, and PH,I [2P + HIAq + 3.1 O = PH, IAq + H, PO, Aq] (Da moiseau, J 1880 272) -8 Conc nitric acid de composes gaseous HI instantaneously -9 Conc. sulphuric acid forms I, and also SO and H S -10 Sulphur dioxide forms S, I, and H,O -11 Iodic acul reacts with IIIAq to form I and H₂O -12 Very many oxidisers separate I with simultaneous formation of H₂O, e g H₁O₄Aq, HClOAq, HClO₄, chromates 13 Many metals form iodides and evolve H, with HIAq -14 Me tallic oxides and carbonates generally form iod ides and H₂O, metallic peroxules form the same products and also separate I -15 HI produces pps of iodides when added to solutions of salts of metals which form insoluble iodides, e.g. salts of Hg, Ag, Cu, Pd -16 Potassium permangan ate produces KIO, -17 HI reacts with carbon compounds generally, especially with such as contain the group OH, as an energetic reducing agent (cf Berthelot, Bl [2] 9, 8, 91, 179, 265)

Combinations—1 HIAq dissolves several metallic volides, e.g. Bil., HgI., PtI., and PtI., some of the solutions thus formed react with alkalis and alkaline hydroxides to form salts, which are probably derived from acids containing I and the metal whose iodide was dissolved in HI., e.g. by dissolving AuI. in HIAq and adding KOH the salt KAuI. is obtained, by similar reactions the salts Na.PtI., MgPtI., &c., are formed Such reactions render it probable that HI combines with many metallic iodides, and that the products frequently r act as acids, one or two such acidic compounds have been isolated, e.g. H.PtI., 9H.O. (cf. Bromhydra Acid), Reaction 7, vol. i. p. 553, and Childhydra Acid, Reaction 13, vol. ii. p. 8)—2 HI combines with ammonia to form NH.I., [NH., HI] = 43,462 (Th., 75)—3 With phosphine HI combines to form PH.I., [PH., HI] = 24,100 (Ogi., C. R. 89, 705)

PH.I., $[PH^2,HI] = 24,100$ (Ogur, C R 89, 705) The solution of HI in water is attended with production of much heat [HI,Aq] = 19,207 (Th.2). IODIDES 13

84) Thomsen's measurements of the heat of solution of HIAq point to the "xistence of a ' ydrate HI HO, the results re similar to those obtained for HClAq, but cannot be represented by so simple a formula (cf CHLOBHY BIG ACID, vol 11 p 8)

The heat produced by diluting II in nH,O with quantities of water varying from 200 to 300 H₂O is given by Thomsen as follows (Th 3,

76) -[HI $nH^2O_1(300-n)H^2O$] 6670 3 4400 1830 5 10 630 20 220 50 70

100 30 The acids H., HBr, and HCl are very similar in their properties and reactions. All dissolve very freely in water, forming solutions of mono ba ic acids, the affinities of which are great and approximately equal All combine with certain metallic haloid compounds, especially with those of Hg, Au, Pt, and Pd, to form compounds which are best regarded as distinct acids. The thermal reactions attending the syntheses of the three acids show a gradation Thomsen (Th 2, 39) gives the following data

Y 'H,X] gaseous, at 180°, from gaseous elements.

Cl 22,153 Br 12,413

I -436

X [H X Aq]

Cl 39 315 Laseous Cl at 19°

Br 32,197 | calculated on assumption that Br 18,619 | and I are gase out at 19

Of the three acids HI is the most easily de composed by heat and by oxidisers (cf HALOGEN ELEMENTS, vol 11 p 605, where HF is compared and contrasted with the other haloid acids HX) MMPM

IODHYDRIN & GLYCERIN

Di-iodhydrin : Di iodo propte alcohol. IODIC ACID t Iodine Oxyacids of p 19

IODIDES Binary compounds of I with more positive elements, ie with any element except O, F, Cl, or Br lodides of almost all metals and binary compounds of I with all non metals except B, have been isolated Most metallic iodides may be obtained by direct combination of the clements, many are obtained by heating I with metallic oxides, or by dissolving netals or their oxides in HIAq, I reacts with alkalis and alkaline hydroxides to form iodides and iodates Some non metallic iodides are formed by direct union of the elements, eq iodides of H, Br, Cl, Se, S, and P, NI, is obtained by the reaction between I and NH, Aq, CI, by the reaction of Al, Iq on a mixture of CCI, and CS, O and I combine indirectly, oxides of I are obtained by the action of oxidisers on I The non metallic iodides as a class are more easily decomposed by heat than the chlorides or bromides, oxide of I is much more stable than oxide of Cl, and no oxide of either Br or F has yet been isolated If two chlorides or bromides of a specified metal are known, the more stable iodide of that metal ide or bromide, eg SbCl, and SbCl, exi t, but

FeI, exists it very easily goes to PeI, and I, similarly with Cul, which exists only in solution, and very readily parts with I becoming CuI, whereas CuCl, is more stable than CuCl. In their eactions with water metallic iodides are usually less easily decomposed than the corresponding bromides and chlorides Metallic iodides as a class dissolve in water without change some, however, form oxylodides, eg SbI, and Bil, and some form oxides and HIAq, eg Snl. Metallic iodides, generally speaking, are not so readily volatilised as chlorides or bromides. most of them are unchanged by heat, but some are decomposed to metal and I, eg nodides of Au, Pt, and Pd As a whole, then, the metallic iodides are not so numerous or so varied in composition as the chlorides or bromides, and they are more stable towards heat and the action of water than the chlorides and bromides, they are also less easily reduced, eg by H or CO, than the chlorides or bromides

The heat of formation of a metallic iodide is usually considerably less than that of the bromide or chloride of the same metal. The following data are taken from Thomsen .-

[Na, X, Aq]Cl 193,020 \mathbf{Br} 171,160 1 140,600 [Ca, X2, Aq] Cl 187,230 Br 165,360 134,940 [Al', X', Aq] Cl 475,650 410,040 I 318,780

The difference between the heat of formation in aqueous solution of a chloride and the ana logous bromide of the same metal is approximately n21,850, and the difference in the case of a chloride and analogous iodide is approximately no2 250 Some metallic iodides ex hibit differences in crystalline form and SG for instance SbI, forms hexagonal crystals, and also exists in trimetric and in monoclinic forms, CdI probably exists as a white salt 5 G 5 644 unchanged at 250, and also as a brownish com pound 5 G 4 626, which begins to change at 40° (t vol 1 p 656), there are also differences be tween Bil, according as it is prepared by sublima tion or by ppn

Iodides are usually decomposed when heated in Cl or Br with production of chlorides or bromides and I, heated in HCl they generally form chlorides and HI Heated with conc H SO, or cone HNO, I is separated, and SO, (also sometimes H S), or NO, is evolved. I is separated from iodides by the action of many oxidising agents, such as CrO, ferric salts, MnO , do

Many metallic iodides dissolve freely in solu tions of the alkali iodides, frequently with formation of double iodides. An aqueous solution of KI dissolves much I, with formation of KI, but the greater part of the I thus dissolved is ppd on largely diluting the liquid Some other periodides analogous to kI, are known, part of as a general rule corresponds to the lower chlor I the I in such compounds .. more loosely combined than the rest, and can generally be reonly SbI., FeOl, and FeCl, are stable, but it moved very easily, CuI, in solution, for instance, 14 IODIDES

is reduced to Cul by shaking with CS. Some iodides, e.g. PtI., HgI., combine with Hi to form compounds which are best regarded as metallic acids (H_PtI., H_HgI., &c) Some of the resemblances and differences between the three allied classes, chlorides, bromides, and iodides, are considered in the article Halogens, Binary compounds of the (vol 1) p 666)

M M P M

IODINE 1 At w 126 53 Mol w 253 06

(v.m/ra) [113°-115°] (Stas), [114 15°] (Ramsay
a Young, C J 49, 460) soludines at 113 6°
(Regnault, J 1856 41), (200°) (Stas), (184 85°)
at 760 mm (R a Y, Ic) Sublimes in vacuo
without melting (L Meyer, B 8, 1627) S G
4 917 at 40 3°, 4 886 at 60°, 4 857 at 79 6°, 4 841
at 89 8°, 4 825 at 107°, 4 004 liquid at 107°,
8 866 liquid at 151°, 3 796 liquid at 170°, vol
mcreases for 1° by 000235 (Billet, J 1855 46)
V D c 250°-1000° 125-127, c 1500° 68 (v
Properties, p 10) S H (solid 9°-98°) 05412
(Regnault, A Ch [2] 78, 1) S H p for I vapour
at 206°-377° (equal wt of water = 1) 03369

(Strecker, W 17, 85), $\frac{S H p}{S H v}$ 1 294 at 220°-375°

(Strecker, W 13, 20) Heat of fusion = 11,710, heat of vaporisation = 23,950 (Favre a Silbermann, A Ch [3] 37, 461) For vapour pressures of solid I from 58° to 114°, and of liquid I from 114° to 185°, v. Ramsay a Young, C J 49, 458 S V S 25 9 S 018 at 10°-12° (Wittstein, J 1857 123), 015 at 6 3° (Dossios a Weith, Z 1869 379) S in glycerin = 1 (Regarding solubility v further under Properties) The absorption spectrum of I vapour shows numerous fine lines extending from the red to the violet thickness of the layer increases absorption be comes very marked in the red, but even when the whole of the red part is obscured, the violet portion remains without bands (Plucker, J 1863 109, Thalen, P 139, 503, cf Conroy, J 1876 146, and Salet, A Ch [4] 28, 29) The emission spectrum shows many bright lines in the zellowgreen and yellow By using an induction cur rent of low tension lines are seen coincident with the dark absorption lines (Salet, lc, Wullner, P 120, 158), at red heat a continuous spectrum is observed I crystallises very easily from alcohol or HIAq, or by sublimation, the crystals are trimetric, $a\,b\,c=4866\,1\,7324$ (Mitscherlich, $B\,B\,1855\,416$)

Iodine was discovered by Courtois in 1811 in the mother liquor of kelp after preparation of Na₂CO₂ Davy (T 1814 74) and Gay Lussac (A Ch 88, 311, 319, 91, 5) showed I to be an element, and established its relationship to chlorine

Occurrence — Certain mineral waters contain small quantities of free I According to Wanklyn (C N 54, 300), the water of Woodhall Spa, near Lincoln, is coloured slightly brown by free I Iodides of Na and Mg, and iodate of Mg according to Sonstadt (C N 25, 196, 231, 241), occur in small quantities in sea-water, alkaline iodides are found in very many mineral waters, in the ashes obtained by burning sea-plants, and some sea animals, and in certain specimens of Chili saltpetre, dolomit, phosphates, and some other minerals Iodides of Hg, Ag, and Pb occur in small quantities in Mexico

Formation—1 By decomposing alkaline iodide. by MnO₂ and H_2SO_4 , or by Cl, or by K_2Cr_2C , and H_2SO_4 , or l. NO_2-2 By heating an acidified solution of an iodide with FeCl₂Aq. 3 By reducin; NaIO₂ by SO_2

 $(^{\circ}AaIO_{2}Aq + 5SO_{2} + 4H_{2}O$ = $2NaHSO_{4}Aq + 3H_{2}SO_{4}Aq + I_{2})$

Preparation — The greater part of the I of commerce is prepared from kelp, which is the product of burning sea plants, the kelp is lixivisted with hot water, and the liquid is eva porated in successive stages until most of the salts except NaI, Na, S, and Na, S, O I ave been ren oved Enough H, SO, is added to decompose the S compounds After exposure to the air for some time S separates and SH, and SO, escape The liquid is then run off and distilled with addition of more H, SO, and M. O, and the I is collected in a series of tubulated receivers buted one into the other For details of manufacture v Dictionary of Applied Chemistry The I obtained as described is dried and sublimed By slow resublimation fairly pure I is obtained, but ICy cannot thus be removed

The chief impurities in commercial I are chlorides, water, traces of various salts, and

sometimes ICy

Stas (Chem Proport 137) gives two methods for preparing pure I -1 KI is dissolved in its own weight of water, the solution is saturated with I (about 4 parts I are required to 1 part KI), water is added until formation of a perma nent pp begins After settling, the liquid is poured off and shaken with 3 of the quantity of water required to bring down all the I which can be ppd by this method (the amount of water is determined by a preliminary experiment on a small quantity of the liquid) The separated I is washed by decantation until the washings are free from K, distilled with water from a large retort, allowed to drain, placed over dry Ca2NO, which is frequently changed (all other drying materials bring impurities into the I), and finally twice distilled after mixing with 5 p c finely-powdered pure BaO The last traces of H₂O and traces of HI are thus removed -2 Niodide is prepared by adding powdered I to cold conc NH3Aq until the dark brown liquid is nearly colourless, the compound is washed by de cantation with cold cone NH3Aq until NH,I is removed, placed on a funnel, the neck of which is drawn to a fine point, and covered with cold water When the black colour of the com pound changes to brownish, and the wash water is coloured yellowish brown, the moist iodide is placed in ten times its weight of water contained in a large glass balloon, and slowly heated on a water bath to 60°-65°, when decom position occurs with formation of crystals of I. solution of I in NH, IAq, and a white salt. which is probably NH,IO, When the change seems completed the liquid is warmed to 100° for a few minutes, if the temperature is at once raised above 65° decomposition occurs very rapidly, at 100° it proceeds with explosive violence, at the ordinary temperature the change is very slow After cooling, the solid which separates is thrown on to a funnel with drawn out neck and washed with water, it is then distilled with water from a retort (NH,IO, is not IODINE 15

volatilised), and the I is dried over Ca2NO,, and finally by distilling with pi re BaO as in

Recovery of 10 .ine from laboratory residues Beilstein (Z 1870 528) recommends to evaporate with excess of Na₂CC₂, to heat the residue until it is white, to add excass of H SO, and to pass in Noxides, obtained by heating starch with HNO, until all I has separated, to wash the I in cold water, dry over P2SO4, and sublime slowly The stream of Noxides is best obtained by adding 15 grams starch to about 90 grams fairly conc HNO Aq in a large flask (the acid must not be added to the starch, else the latter may cake on the bottom of the flask and cause it to break), heating till red fumes appear, and then removing the flame and cooling from time to time, if necessary, by cold water If insoluble iodides, eg HgI₂, are present, Henry (B 2, 599) heats with water and granulated Zn or Fe filings, whereby soluble ZnI2 or FeI2 is produced final sublimation of the recovered I may con veriently be conducted as described by Mohr The rim of a flat porcelain basin is ground with sand, so that a glass plate placed on the basin touches the r'm in every part, the I is placed in the basin, a little finely powdered KI is strewed on the surface, the glass plate is placed in position and bound to the rim by a strip of paper, and the basin is placed on a sand tray and very slowly heated The process of sublimation should occupy several days If any ICl is pre sent it reacts with the KI to give I Cl and I

Properties —A greyish black, soft, solid with metal like lustre Perfectly pure I is described by Stas as quite black, whether solid or liquid Only the thinnest plates of I are transparent (cf Schultz Sellack, P 140, 334) I is very easily vaporised, the vapour corrodes the skin and mucous membranes, unsaturated vapour has a violet colour, saturated vapour appears deep blue in thin layers (Stas), a layer 10 centims thick is quite impervious to light (cf Andrews, C N 24, 75) I vapour shows orange yellow fluor escence (Lommel, W 19, 356), solid I does not fluoresce (Stokes) Crystals of I polarise light (Conroy, J 1876 147) I is a non conductor of electricity (Jolly, P 37, 420) I dissolves freely in solutions of alkaline oxides and in HIAq. it is more soluble in solutions of NH, salts than in water Dossios a Weith (Z 1869 379) give the following numbers for the S of I in KIAq

	P	c.		1	P.c.	
S.G at 7 90	KI	1	S.G at 7 9		1	
1 0234	1 802	1 173	1 1382	8 663	7 368	
1 0433	8 159	2 303	1 1637	10 036	8 877	
1 0668	4 628	8 643	1 1893	11 034	9 949	
1 0881	5 935	4 778	1 2110	11 893	11 182	
1 1112	7 201	6 037	1 2293	12613	12 060	

I is more soluble in solution of tannic acid than in water, addition of 015 parts of the acid in creases S to 42 at c 30°, and when 33 parts acid are present S is 24 at 12° (Koller, Z 1866 880) I is very sol in CS₁, CHCl₁, ether and alcohol, C₂H₂ and various hydrocarbons, also sol in SO₂ (Sestini, Z 1868 718), and in SO₃ (Weber, J pr 25, 224), solutions in ether or alcohol contain HI (cf Carles, Ph [3] 5, 89) Addition of CS₂ to an aqueous solution of I causes withdrawal of most of the I from the water, according to Berthelot a. Jungfleisch

c 400 parts of the I go into solution in the CS₂ for each part remaining in the water (C R 69, 338) Solutions of I in CS₂, CHCl₂, C_cH₆ and other liquid hydrocarbons are violet, solutions in ether, alcohol, and some other solvents are reddish brown. The reddish solutions absorb light in the violet end of the spectrum up to midway between D and E, cone violet solutions absorb the rays of mean refrangibility to the limits of the yellow and blue, very cone solutions absorb all rays except the ultra violet (cf. Vogel, B 11, 919)

The at w of I has been determined —1 By changing AgI into AgCl (Berzehus, P 14, 558, Dumas, J 1859 3)—2 By synthesis of ZnL (Gay Lussac, A Ch 91, 5)—3 By synthesis of AgI (Marignac, Bibl Univ Genève, 46, 367, Stas, Chem Proport)—4 By determining the quantity of KI required to ppt a known quantity of Ag dissolved in HNO. (Marignac, lc)—5 By analysis of AgIO. (Stas, lc)—6 By determining V D of many binaly compounds—7 By measuring S H of I

Attempts have been made to determine themol w of I in solution Paternoa Nasini (B 21, 2153) measured the lowering of the freezing point of benzene and acetic acid produced by dissolving I in these liquids, the results point to the existence of molecules of I, in very dilute benzene solutions, and more complex molecules in more cone solutions, the numbers got with acetic acid lead to a mol w between I and I. Loeb (C J 53, 805) determined the vapour pressure of I in solution in CS, and ether, ethereal solutions of I are reddish brown, solutions in CS, are violet, Loeb's results point to the mol w I, in red solutions, and a mol w between I, and I in violet solutions

Determinations of the S G of I vapour, by Gay Lus-ac, Dumas, Bineau, Deville a Troost, up to c 1000° gave values from 878 to 862 (calc for $I_a = 8.75$) V Meyer (B 13, 401, 1723, 14 1453) ob tained the following results -8 86 at 293°, 8 72 at c 586°, 6 76 at c 842°, 5 75 at c 1027°, 5 7 at c 1570° Crafts a Meier (B 13, 870, C R 92, 39) obtained similar results, the SG remained con stant (88) to c 700°, even when pressure was diminished, but decreased above that tempera ture, and decreased the more rapidly the more the pressure was lowered, the SG decreased with rising temperature rapidly to a certain point and then more slowly, at a pressure of 230 mm SG became constant at 1400° - 1500° and was = 46, at 152 mm SG became constant at c 1400°, at 76 mm a constant value for SG was obtained at c 1350° At c 1700° V D corresponds with molecular weight = I (Biltz a Meyer, \hat{B} 22, 725) There can be little doubt that these results prove a gradual dissociation of I2 into I (S G calc for I=4 375) (cf Dissociation, vol 11 p 394, v also Naumann, B 13, 1050) The molecule I_2 is more easily dissociated than either of the molecules Br, or Cl, The atom of I is monovalent in gaseous mole

The atom of I is monovalent in gaseous mole cules I acts as a non metallic element, it is negative to all elements except O, F, Cl and Br I combines directly with most of the metals, and with some of the non metals, eg H, Br, Cl, Se, S, and P, binary compounds of I with all non metals except B have been isolated I is closely related to F, Cl, and Br, the relationship is con

16 IODINE

sidered in the article Halogen elements, vol 11 p 664, of also Indines in this vol p 13

Reactions -1 I dissolves very slightly in water, the solution probably contains traces of HI According to Cross a Higgins (C J 35, 225) I dissolves slightly in water at 100° in a sealed glass tube with production of a little alkaline iodide and iodate Electrolysis of IAq yields HIO, Aq (Riche, J 1858 101)—2 I does not react directly with oxygen, even when I and O are heated to c 300 in presence of spongy Pt (Wehsarg, B 17, 2896) Ogier (C R 86, 722) sa s that if I vapour and O are subjected to the suent discharge, all the oxides of I are pro duced -3 Hydrogen peroxide produces HIAq and O, but conc HIAq is decomposed by HO2 with separation of I-4 Hydrogen sulphide is decomposed by I in presence of water forming HI and S, dry H2S does not react with I-5 With solutions of caustic alkalis, I forms alka line iodide and iodate, according to Van Deventer a Van't Hoff, KIO is also formed (the proof of this is indirect, C C 1888 362) -6 Ammonia gas forms NH, I and N (v Combinations, No 2), ammonia solution forms NH, IAq and N iodide 7 When I is shaken with lime suspended in water, a bleaching liquid is obtained which re acts as if it contained Ca hypoiodite Ca(IO) and CaI, (Lunge a Schock, B 15, 1883) -8 I va pour heated with oxides or carbonates of the alkaline earth metals, in presence of oxygen yields periodates without formation of oxy iodides, with lead oxides various oxyiodides are prod ced 'Cross a Sigiura, C J 33, 405) -9 I is oxidised to I2O3 by nitric acid, chromic anhydride, chlorates, and some other oxidisers -10 I in presence of water acts as an oxidiser towards some salts and other easily oxidised compounds, arsenious oxide and arsenites are oxidised to As₂O₅ and arsenates in alkaline solu Sulphurous acid is oxidised to H,SO sodium throsulphate is oxidised to Na S4O4 and a little NaHSO₄ (Pickering, C J 37, 128) —11 With some carbon compounds I reacts to substi tute I for H, but the HI formed tends to repro duce the original compound, so that the reactions of I with C compounds are much less marked than those of Cl and Br -12 I dissolved in CS, reacts with ppd arsenious sulphide (not with orpiment) to give AsI_3 and S, at a higher temp As_2S_3 and I are reformed, by distilling As_2S_3 and I in the ratio As, S, 6I and heating the dis tillate in a sealed tube to 72° (AsI₃)₂SI₄ was ob tained (Schneider, J pr [2] 36, 498)

Combinations —No combination of I with H_2O has been isolated —1 With most metals, and with many non metals, especially with H, Cl, Br, S, Se, P, As According to Holzmann (B 22, 869) Na is scarcely attacked by I when the pure elements are heated to 300° Fe and Icombine by shaking Fe filings with I in presence of water, FeI2 is produced, and also Fe2O3 and HI probably by the formation and decomposition of FeI₃ (Fleury, J Ph [5] 16,529) -2 Ammonia forms several compounds with I, the dry gas isabsorbedformingadark blueliquid, the volume of NH₃ absorbed varies with temperature, at 20° 1t corresponds to 3NH, 2I, at 80° to NH, I, at 0° to (NH_s), I, at -10° to (NH_s), I₂ (Raschig, A 241, 253, cf Bineau, A Ch [3] 15, 80, Millon, A 62, 54)

Detection and Estimation —Free I is detected in solution by the colour which it gives to CS, or CHCl, and by the formation of a deep blue colour when a drop of starch paste is added (cf Béchamp, Fr 14 66, Mylius, B 20,688, Personne, *C R 74,617, Duclaux, C R 74,533, Goppels-röder, P 119, 57, Hlasiwetz, W A B 1867 I in soluble iodides is detected by adding a very little Cl water, or a drop of a solution of NO2 in conc H2SO4, and then a little starchpaste Iodates are reduced to iodides by SO.Aq. alkaline iodates mixed with all aline iodides and a drop of a weak acid, eg tartaric, give free I Many insoluble iodides may be converted into soluble ZnI by treatr ent with Zn and dilute H,SO,Aq Most non metallic iodides are decomposed by water or critic alkali giving HI or alkaline iodide I is estimated gravim trically by ppn as AgI, iodates are reduced by SO Aq and then ppd by AgNO, Aq Volumetrici'ly I is estimated by titration with standard Na₂S₂O₃Aq, or standard As₂O₈ dissolved in NaHCO,Aq The water in samples of ordinary I may be determined by mixing with a weighed quantity of Hg, rubbing up with a little alcohol, and carefully drying at 100°, loss of weight = water (Bolley, D P J 126, 40) The quantity of I may be determined by dissolving in a cone solution of an alkalı sulphite, filtering, ppg by AgNO, Aq, washing pp with NH, Aq to remove AgCl and AgBr, boiling with H,O containing a little AgNO, to remove Ag SO, washing the residual AgI, and weighing it, after drying, in

the usual manner (Hesse, A 122, 225)

Iodine, bromides of Two bromides of I are known, IBr and IBr,, but neither has been gasified, attempts to prepare IBr3, analogous to ICl₃, have failed (Bornemann, A 189, 183) The combination of I with Br has been studied by Balard (A Ch 32, 337), Lagermark (B 7, 907),

and Bornemann (A 189, 201)

IODINE MONOBROMIDE IBr Formula not necessarily molecular, but probably so, from analogy to ICI which has been gasified Prepared by heating I with rather more than the calculated quantity of Br to 25°-50° in a retort, removing excess of Br by a stream of CO,, and allowing to cool Forms dark greyish, iodine like crystals, melting at 36°. probably sublimes with only partial decomposition, smells of Br, the vapour attacks the eyes and mucous membranes The vapour appears red in thick strata (Gernez, C R 74, 1190) Soluble in alcohol, CHCl3, CS2, and ether, slowly decomposed by water with separation of I Berthelot (A Ch [5] 21, 370) gives the H F of solid IBr from solid I and liquid Br as [I, Br] = 2470 A hydrate IBr 5H O described by Lowig is merely a mixture of IBr and ice

Iodine pentabromide IBr. A dark brown liquid obtained by heating excess of Br with I, soluble in water, with alkali solutions forms bromide and iodate, solution in sunlight decomposes to HBr and HIO,

Iodine, carbide of, better called Carbon iodide, v vol 1 p 689

Indices I combines rapidly with Cleven at -90° (Donny a Mareska, CRTwo chlorides of I have been isolated,

ICl and ICl,, ICl can be gasified without decom position, iCl, decomposes when heated Kam merer (J pr 83,83, cf B 8,489, note) asserted

the probable existence of a tetrachloride ICl., but the non existence of this compound has been proved (cf. Hannay, C. J. 35, 169), Brenken (B. 8, 187) failed to procure any higher chloride by passing Cl. over strongly cooled ICl. By adding I to liquid Cl. Hannay (~J. 35, 169) obtained a reddish liquid when the elements were present in the ratio I. 5Cl, but on removing pressure or raising temperature Cl was at once evolved.

IODINI MONOCHIORI & ICL Mol w 1619 [212], (1013), S.G. & 318223 (Thorpe, C.J. 37, 174, II.F. [I, Cl] = 2,100 (solid ICl from gaseous Cl and solid I), 6,700 (solid ICl from gaseous constituents) (Berthelot, A. Ch. [5] 21, 370) V.D. & 9.29 at 120° 83 2 at 512° (Hannay, C.J. [2] 11, 819) Absorption spectrum of vapour v. Gen. J., C.R. 74, 660

Preparation -1 By passing dry Cl over carefully dried I till liquidiction occurs and I infring by distillation with a gram or two of I 2 By heating an intimate mixture of I with 4 parts KclO₃ and distilling the preduct from powdered KClO₃ (I₂+3KclO₃ KclO₄+KlO₄+KCl+O₂+ICl) - 3 By boiling

KelO₄+ kIO₄+ kCl + O₂+ ICl) - 3 By boiling I with excess of aqua regue diluting with water, shaking with ether and evaporating the ethereal liquid (Bunsen, A Si, I)

Properties - ICI seems to exist in two forms, a reddish brown oily liquid (Gry Lussie, 1 Ch 91, 5), and a hy centh red solid (Schutzenberger, 2 5, 1) Thorpe (C J 37, 175) says that ICI remains liquid in a closed vessel for weeks even in a freezing mixture but solidities on addition of a minute frigment of ICl, If the liquid ICl is exposed to the ur it solidifies after a time and is partially changed to ICl, and I (cf. Hannay, C. J. [2] 11, 815, hornemann, 1, 189, 183). According to Stortenbeker (R. T. C. 7, 152), two forms of solid ICl exist one forming dark red needles melting c 27° obtained by cooling the liquid ICl to -25° , and another crystallising in dark red plates melting at a 14° obtained by crystallising the liquid between -10° and +5° ICl smells of I and Cl, it ittacks all mucous membranes rapidly and forms very bad sores if let fall on the skin, decolourises indigo, does not give blue colour with starch (cf Christomanos, B 9, 131) ICI dissolves in alcohol, also in HClAq C in be distilled with only very slight decomposition (Schutzenberger, Z 5, 1, cf Bornemann, A 189, 183)

Rea tions—1 Water decomposes ICl forming HCl, HIO₂, and I (Hanna), C = J = 11, 9.20)
According to Schutzenberger (lc) a compound ICl HCl is formed (besides HIO₂ and I) by the reaction of water with ICl (cf also Tripp, J = 1854 = 310), and Bornemann, 1 189, 181)—2 Potash solution produces KIO₂ and KI with separation of I (H, lc)—3 Ammonia solution forms NII,Cl, and N iodide which combines with a portion of the NH, (Bunsen, A = 84, 1)—4 Distilled repeatedly with potassium iodide, KCl and I are formed—5 Dissolves in carbon disulphide, when a saturated solution is distilled CCl₄ and CSCl are formed (H, lc)—6 With many metals ICl reacts to form chlorides and iodides (H, lc), cg with Hg, Sn, Sb, Bl, Al, Mg, Na—7 With mercuric oxide, cupric oxide, and lead peroxide, founs chlorides and iodides

with evolution of O and separation of L—8 Hypochlorites and chlorates produce iodates with evolution of Cl (Henry, B 3, 892)—9 Mercuric cl loride forms a pp of HgI₂ (Kane, J pr 11, 250)—10 Stannous chloride produces SnCl₄ and SnI

Combination —With hydrogen chloride to form HCl ICl, a yellow, volatile, unstable compound, produced by dissolving ICl in water, extracting with ether, and evaporating (Schutzenberger, C R 84, 389)

IODINF TRICHLORIDE ICl, Mol w unknown, decomposed by heat to ICl and Cl S G c d 1107 (Christomanos, B 10, 789) [25°] (Trapp, J 1854 310), [33°] (Christomanos, lc) H F (Berthelot, A Ch [5] 21, 370) [I, Cl³] = 21,700 solid ICl, from gaseous constituents, 16,300 solid product from solid I and gaseous Cl, [ICl, Cl²] = 9,500 solid product from solid ICl and gaseous Cl According to Brenken (B 8, 487) ICl, is partially decomposed when it is melted Stortenbeker (R T C 7, 152) gives M P as varying from 20° to 60°, but says that at pic source of 16 atmos the M P is definite and = 101°

Preparation -1 By leading excess of dry Cl over I or ICl until yellowish red crystals are formed, and then subliming at as low a tem perature as possible in a stream of Cl (Brenken B = 8 + 1.7) - 2 by the action of HCl on warm powdered HIO, Clis evolved (Ditte, A 156,335) By the action of PCl, on IO, -1 Christo manos (B 10, 134, 789) recommends to lead dry Cl and dry HI into a well cooled glass receiver, keeping the Cl in excess (HI + $4Cl = HCl + ICl_1$, if HI is in excess the reaction $HI + ICl_s = HCl + 2ICl$ occurs) Io prepare small quantities of ICl, say in a bulb tube Christomanos leads dry Cl through the tube, cools the place where the ICl, is to be deposited, then allows dry HI to stream through the tube, and finally leads dry Cl again, all parts of the apparatus being gently warmed except that where the ICl, is to be formed

Properties - A citron yellow, crystalline, deliquescent solid Very disagreeable smell, attacks the eyes and nose Can be kept un changed only in dry Cl (Hannay, Christomanos) In air sublimation with partial decomposition begins even at -12 (C) Complete decomposition into ICl and Cl occurs at c $70^{\circ}-80^{\circ}$, even in an itmosphere of Cl at pressure of 760 mm (Melikoff, \vec{B} 9, 490) According to Brenken (B 8, 187) ICl, does not melt when heated, but decomposes even in an atmosphere of Cl into ICl and Cl at c 25°, the temperature varying according to the pressure ICl, is sol water, with pritial change to ICl, HCl, and HIO,, at 100° this change occurs suddenly and completely (Bornemann, B 10, 121, Christomanos, Ic) Sol benzene, sol conc H2SO4

Reactions—1 With water to form ICl, HCl, and HIO,, in cold water a part of the ICl, remains unchanged, in hot water the change is complete, at 100° it occurs very rapidly—2 With caustic all alis, chloride and iodide, chlorate and iodide, of the alkali are produced (Christomanos, lc)—8 With excess of ammonia, NH,Cl, NH,I, and NI, are formed (C)—4 itric acid produces Cl and I (C)—5 Hydrogen iodide in excess forms ICl and HCl (C)—6 Carbon disulphide produces some 8 chloride, the solution contains

C

SI, xI (0) (cf Weber, P 128, 459) -7 Carbon dioxide passed over ICl, forms a little COCl, (C) 8 ICl, Aq shaken with silver oxide forms AgĆl and $\mathring{H}\mathring{I}\mathring{O}_{s}$, heated with excess of $A_{b}O$, A_{g} periodate (Philipp, B 3, 4) -9 Hydrogen has no action at the ordinary temperature, when the ICI, is slightly warmed HCl+ICl are produced, at a higher temperature HCl, HI, and I are obtained (U) -10 Potassium and phosphorus burn in ICl₃, forming chlorides and iodides (C) -11 ICl₃ oxidises hot sulphurous acid solution to SO₂Aq, and hot ferrous sulphate solution to ferrie sulphate (C)—12 On carbon compounds the action of ICl₂ is to chlorinate, e.g C₂H₄O₂ even in the dark forms C₂H₃ClO₂ with simultaneous production of HCl and ICl

Iodine, cyanides of Better called Cyanogen todide, v vol 11 p 813, and Cyanuric todide,

e vol n p 320 Iodine, fluoride of IF, A colourless, strongly smelling and fuming liquid, does not solidify at -20°, obtained by decomposing AgF by I Attacks glass and Si at red heat, no action on Hg or Pt, decomposed by water to HIO, and HF (Gore, C N 24, 291, MacIvor, C N 32, 232)

Iodine, hydride of, v Iodhydric acid, p 11 Iodine, nitride of Better called NITROGEN **IODIDE** (q v in this vol)

Iodine, exides of The only exide of I which has been certainly isolated is I_2O_5 , the existence of IO2 is probable Other oxides have been c.scr. ed, but the proofs of their isolation are very meagre I and O do not combine directly, Wehsarg (B 17, 2896) passed I and O over spongy Pt heated to c 300° without obtaining any compound According to Ogier (C R 86, 722) when a mixture of I vapour and O is submitted to the silent electric discharge all the oxides of I are produced I₂O₅ is the anhydride of HIO, which acid is known as a definite stable solid, IO₂ (if it exists) is not an anhydride, it is said to combine with H₂SO₄. The hypothetical anhydride of periodic acid, I₂O₇, has not been isolated The heat of formation of I_2O_8 is a large positive quantity = c 45,000 I_2O_3 is a much more stable body than any of the oxides of Cl, no oxide of Br or F has been isolated

IODINE PENTOXIDE LO. (Iodic anhydride)
Mol w. unknown, as oxide has not been gasified SG -4487 (Ditte, A Ch [4] 21, 5), SG -90 47987 (Kammerer, J pr 79, 94) CE 0°-51° -000066 HF from solid I [I2, O3] = 45,029, [I², O³, Aq] = 43,237, [I²O⁵, Aq] = -1,792 (Th. 2, 164) S = 187 4 at 13°, S G of this solution = 2 1269 (Kammerer, P 138, 390) A white crystalline solid, crystals belong to trimetric system (Schabus, J 1854 310) Produced by slowly heating dry HIO, to 170° Melts when heated to c 300°, with decomposition into I and When HIO, crystallises from solutions con taining H2SO4, crystals of I2O4 are said to accompany the HIO, (Rammelsberg) Sol water, insol ether, alcohol, CHCl, CS, or C,H, (Ditte, C R 70, 621) LO, dissolves in water to form HIO. The general reactions of LO, are those of an oxidiser. CO passed over warmed I₂O₅ forms CO, and I, SO, gives SO, H₂S produces HI, H₂O, S, and I, HCl forms ICl, and H₂O, NH,

does not react with LO, (Kammerer, J pr. 79, 94)

Combinations -1 According to Kammerer $(J \ pr \ 83, 72)$ when dry SO_2 is passed over I O_4 heated to 100° a part of the SO_2 is oxidised to SO₃, a little J seing separated, and then a yellow crystalline compound 5I O, SO, 18 formed soon as the compound is formed the SO, must be stopped The compound is decomposed by mois ture, even by exposure to ordinary air (C R 70, 621) says that in this reaction only I and SO, are produced According to Weber (B 20, 87) the compound I,O, 38O, is formed by heating the constituents in a sealed tube to c 60°, and pouring off excess of SO₃, the compound is decomposed above 60° -2 By heating HIO, slowly to 30°-40, or more quickly to 130°, the hydrate 31,0, H2O is said to be formed Ditte, however, says this is only a mixture of I.O. and HIO,

Nitroso derivative (?) By treating perfectly dry finely powdered I with c 10 times its weight of the most conc HNO, Aq, or a mixture of equal parts of cone HNO, Aq and H.SO,, a loose flocculent yellow powder is obtained This sub stance was regarded by Millon (J pr 34, 319) to be a compound of I, O, and HNO₃, according to Kammerer (J pr 83, 65) it is I2O4(NO)2, but no analyses are given The substance is extremely unstable, it cannot be dried over CaO without decomposition it is decomposed by water to HNO, HIO, and I Heated in CO, NO, and

I₂O₄ are formed
Iodine dioxide or tetroxide IO₂ or I₂O₄ This substance probably exists as a definite compound One part of perfectly dry I is rubbed in a basin with 10-12 pts conc HNO, Aq S G at least 1486, until a loose flocculent yellow powder is produced (v supra), excess of soid is poured off, the powder is placed in a funnel stopped with asbestos, and is then died on a porous tile, and finally over lime, HIO, and I are then removed by washing with water and then with alcohol (Millon, J pr 34, 319, 337) IO, is described as a sulphur yellow powder, unchanged in air, decomposed to I and HIO, by heating in air to 170°-180°, insol cold water, but decomposed by boiling water giving I and HIO₃, not acted on by alcohol Warm HNO₃ produces HIO, and I, but H.SO, dissolves the substance, and on cooling crystals of H.SO. IO. separate, HClAq forms ICl and Cl, aqueous alkalı solutions produce iodates, but alcoholic solutions of alkalis are said to form red liquids containing very unstable compounds

Other compounds of rodine and oxygen have been described, but it is very doubtful shether any definite compound except I_2O_5 and probably IO_2 has been isolated. By the action of ozone on I, Andrews a Tait obtained a yellow powder. supposed by some chemists to be I₂O (A a T Pr 9, 608, no analyses given) Ogier (C R 85, 957) asserted the formation of I₂O₂ by the action of ozonised O on I, he described it as a yellow deliquescent powder, decomposing at 125°and I with evolution of I and O, giving HIO, and I with water Millon (J pr 84, 336) supposed he had obtained I₁₀O₁₉ by exposing to moist air the preduct of boiling I₂O, with cone H₂SO₄ H₂O, S, and I, HCl forms ICl, and H₂O, NH, until both I and O were coming off. Kammerer, on heating gives H₂O, N, and I (Ditte, i.e.). NO | (J pr. 83, 78) treated I₂O, with SO, and by

washing the product with alcohol and vater ob tained a brownish 'sllow powder supposed to be I₂O₁. These substances were probably mixtures Bengieser [in 1836] (A 17, 2°4) says that by heating H,IO₂ (v Periodic acta; to 160°; it loses water, and that at o 180° O is e. lived and I₂O₃ remains, possibly I₂O, may be formed at c 160°; but Rammelsberg (J pr 103, 278) says that decomposition of H,IO begins at 133°, and Lang lois (J pr 56, 36) puts the decomposition tem perature at 130°

Iodine, oxyacids of. The only oxyacids of I which are certainly known are HIO, and H, IO, both are solids There are indications of the existence of HIO in aqueous solution, but neither this acid nor any of its salts has been actually isolated The periodic acid corresponding with HClO, has not been isolated, but many salts of the form MIO, are known, the periodates form several complex series of salts whereas all the per HIO, 18 hlorates belong to the series M'ClO. a product of the action of many oxidisers on I, eg HNO, Cl in presence of H₂O, KOHAq This acid or ar iodate is also formed by digesting MgO, HgO, or Ag O with I and H2O, or by shak ing up AgNO, with an alcoholic solution of I Electrolysis of IAq or HIAq yields HIO, Iodides dissolved in water are oxidised by KMnO,Aq, and by bleaching powder, to iodates HIO, is produced by heating solutions of HClO₃, HClO₂, HClO, or HBrO₃ with I If the e reactions are compared with those whereby bromic and chloric acids are obtained (vol 1 p 537, and vol 11 o 15) it is seen that it is more easy to pass from less oxidised, or non oxidised, compounds of I to HIO, than from corresponding compounds of Cl or Br to HClO, or HBrO. The heat of formation of HIO, is much greater than that of HI, whereas the heats of formation of HClO, and HBrO, are considerably less than those of HCl and HBr -[H, I, Aq] -13,170, [H, I, O, Aq] = 55,800 (cf vol 11 p 605) Periodic acid and its salts are stable compounds, they are more readily formed by oxidation pro cesses then perchlorates, eq passing I vapour with O over heated BaO produces Ba periodate, and passing Clinto an alkaline iodate in presence of alkalı produces an alkalıne periodate anhydride of iodic acid, I₂O₃, is known as a stable solid, but the anhydride of periodic acid, I2O, has not been isolated (1 supra, Iodine, oxides of)

Detection and estimation of sodates and periodates - Iodates are detected by mixing with an alkaline iodide, adding a little starch paste, and a few drops of a weak acid, eg tar taric acid, when I is set free and colours the starch blue Periodates give a brown pp of AgIO, on addition of AgNO, in presence of HNO. Periodates may be separated from iodates by ppg both as Ba salts and digesting pp with NH, carbonate, when Ba periodate remains unchanged, but the iodate is converted into BaCO, Iodates may be estimated by reduction to iodides by means of SO, or SH, and ppn with AgNO,, or by digesting with KI and a little HCl, when Cl is set free and decomposes the KI, giving free I which is determined volu metrically Periodates may be estimated by a similar method (A Kimmins, O J 51, 301)

Hypo monous acm and Hypo-monres Neither the acid nor any of its salts has been isolated,

According to Köne (P 66, 802, Lippmann, B 7, 1773) the solution obtained by shaking an alcoholic solution of I with ppd HgO probably contains hypo iodous acid, but this acid quickly decomposes to HIO, and I When I is added to KOHAq or NaOHAq a yellowish liquid is obtained, which bleaches indigo, gives a blue colour with starch, and is decomposed by H2O2Aq with evolution of O, on heating, iodide and iodate are This solution probably contains KIO or NaIO (Schönbein, J pr 84, 337, Berthelot, B 10, 900, Van Deventer a Van't Hoff, C C 1888 362) Lunge a Schock (B 15, 1883), by the action of I on CaO suspended in water, obtained a colourless solution which bleached logwood, litmus, and cochineal, gave no colour with starch, addition of acids separated I, H2O2Aq caused evolution of O, the solution decomposed slowly in the dark, more rapidly in sunlight, but even on boiling for some hours it was only partially decomposed L a S suppose this solution to contain an I compound, analogous with bleaching powder, probably Ca OI I

IDDIC ACID, and *Iodates* HIO₃, MIO₂ The acid seems to have been first obtained by Connel by oxidising I by cone intric acid (New Edin Philos Journ 10, 93, 337, 11, 72, 13, 284)

Occurrence — Sometimes in commercial nitric acid (Pettenkofer, J 1857 581)

Formation -1 By oxidising I by very conc HNO, Aq, or by HBrO, Aq (Kammerer, J 79, 94), or HClO, Aq (Davy, S 11, 68, 234, 16, 343) -2 By decomposing Ba(O₃) by the proper quantity of H SO, Aq -3 By suspending AgIO, in water, adding an equivalent quantity of I, filtering from AgI, and evaporating to dryness $(10\text{AgIO}_2 + 12\text{I} + 6\text{H}.O + \text{Aq} = 12\text{HIO}_2\text{Aq} + 10\text{AgI}$, Kammerer, P 138, 390) The AgIO, is prepared by ppg NH,IO, by AgNO, and the NH,IO, is made by digesting Ba(IO₄), with solution of NH, carbonate—4 By digesting an aqueous or alcoholic solu tion of AgNO, with I (10AgNO, Aq + 12I + 6H O = 10HNO,Aq + 10AgI + 2HIO,Aq, Lassaigne, J Chim méd 9,508, Weltzien, A 91, 43) -5 By decomposing KlO, Aq by H, SiF, Aq, filtering, and evaporating to dryness, the product is impure -6 By leading Cl into water containing I in suspension, the greater the dilution the greater the quantity of Cl required to change all the I into HIO, (of Bornemann, A 199, 183, Sodini, B 9, 1126) -7 By electrolysing solution of I or HI (Riche, C R 46, 348) -8 By the action of Au,O, on I in presence of water (6I + 5Au₂O₃ + 3H₂O + Aq = 6HIO₂Aq + 10Au₃, Colin, G A 48, 280) -9 By moistening ICl₂ with a little water and then shaking with ether or alcohol (Liebig, P 24, 363) -10 Alkaline iodates are obtained by acting on I with caustic alkalis, or by oxidising alkaline iodides by KMnO Aqor solution of bleaching powder (Hempel, A 107, 100, Reinige, Fr 9, 89, Reichardt, Ar Ph [3] 5, 109 KIAq+2KMnO₄+H₄O $= KIO_2Aq + 2MnO_2 + 2KOHAq,$ 2KIAq + 6CaOCl2Aq

= Ca(IO₂)₁ + 5CaC(I,Aq + 2KCIAq) —11 Hg(IO₂)
18 obtained, along with HpI₂, by shaking I with
ppd HgO suspended in water (Colin, G. A 48

Preparation —1 About 5-10 grams finely powdered I is placed up a large flask, twice it

weight of cone nitric acid S G 15 (not furning acid) is added, and the bottom of the flask is gently warmed, the I is gradually oxidised, by keeping the upper parts of the flask cool any I which volatilises is prevented from escaping After a time the acid becomes diluted, it is then poured off, fresh acid is added, and the oxidation is continued until the whole of the I has been converted into white crystals of HIO, greater part of the acid is poured off, the semi-liquid mass is evaporated to dryness in a basin, and the remaining acid is removed either by repeated evaporations with water or by heating to 100°-130° in an air current The crystalline mass may be dissolved in water and slowly evaporated to the crystallisation point, and the crys tals heated to 170° -2 Two pts cone H2SO. and c 8 pts water are added to 9 pts finely powdered Ba(IO,)2, the whole is boiled for half anhour, after settling, BaSO, is removed by filtration, and the filtrate is evaporated until HIO, separates on cooling, the crystals are dissolved in water, a very little Ba(IO₃)₂ is added, and the liquid is evaporated and filtered Stas says that pure HIO, cannot be obtained by this me thod, the crystals always contain either $Ba(IO_3)_2$ or H_2SO_4 The $Ba(IO_3)_2$ required may be prepared (1) by adding BaCl, Aq to NaIO, Aq obtained by passing Cl into water containing I in suspension, till the I is all dissolved, then adding Na,CO, till neutral, and again passing in Cl (Liebig, P 24, 363), (2) by suspending I in hot sat rated BaOAq and passing Cl into the liquid (Kammerer, J 1860 94), (3) by adding tather more than the equivalent quantity of I to hot cone KClO, Aq, and then a few drops of nitric acid, Cl is freely evolved, and KIO, crystallises on cooling, the salt is recrystallised once and decomposed by BaCl₂Aq -3 NH₄IO₄ is prepared by digesting Ba(IO₃), with NH, carbonate solution, filtering, and crystallising, AgNO₃Aq is added to a solution of the NH₄IO₃ and the AgIO, obtained is collected and washed, the AgIO, is suspended in water and I is added in the ratio of 1 gram to 1 857 grams of the AgIO,, the reaction $10 \text{AgIO}_s + 12 \text{I} + 6 \text{H}_2 \text{O} = 12 \text{HIO}_s + 10 \text{AgI}$ proceeds when the liquid is warmed on the water bath, AgI is removed by filtration and the liquid is evaporated to dryness and the residue heated to c 170° (Kammerer, P 138, 390)

Properties—HIO, forms colourless tilmetric crystals, a b c = 589 1 1 1903 (Rammelsberg, P 90, 12), a b c = 9388 1 1 3181 (Schabus, J 1854 310) It is doubtful whether HIO, shows dimorphism or not (v Rammelsberg, Handbuch der Krystall-physikal Chemie, 1 41) Thomsen gives the following thermal data (Th 2, 163)—[H, I, O³] = 57,963, [HIO³, Aq] = -2,166, [I²O³, H²O] = 2,540 S G 2 4 629 (Ditte, C R 70, 621) Very soluble in water, most conc solution, according to Kammerer, contains 68 51 pc HIO₃, boils at 100°, and has S G 2 1629 Kammerer gives the following table—

S G at 14° 1 4428 S.G at 14° Po HIO, 1054 Pc HIO. 1 0058 36 89 1 0263 5 27 1 5371 42 16 1 0525 10 54 1 6315 46 98 1 1223 15 8. 52 70 17356 1 2093 21 08 1 8689 57 97 12,73 26 35 19954 63 24 1 3484 81 62 2 1269 68 51

Thomser has determined the volume change attending the dilution of HIT, Aq He expresses

It by the formula $Va = 18a + 39 \left(1 - \frac{a}{a+18} 13 1\right)$; the composition of the solution is represented by HIO₃ aH_2G , the volume of one molecular weight of water is taken as 18 For optical properties of HIO₃ crystals v Lang, W A B. 31 SH of HIO₃ = 1625 (Ditte, A Ch [4] 21, 52) Electrolysis of HIO₃ produces I and O (Magnus, P 102, 1, Buff, A 110 257)

Reactrons—HIO, reacts as an energetic oxidiser 1 Most non metals are oxided by HIO, \(\hat{A}\)Q, eg P to H3PO As to H3ASO, B to HBO, \(\hat{S}\) is at 250° to SiO2 (Ditte, Bl 1870 318), S, Se, and C are oxidised by heating in scaled tubes with HIO3AQ, S to H2SO, Se to H2SO, gas coke at 180° and anthracite a 210° to CO, diamond is not acted on—2 All metals, except the Pt metals and Au, are oxidised by HIO3AQ—3 Sulphurous acid is oxidised to HSO, sulphuroted hydrogen to S and HI, the lower oxides of nutrogen to HNO3—4 Hydrochloric acid forms ICl, and Cl

Combinations—1 With water to form 2HIO₃ 9H₂O, obtained by cooling saturated HIO₃Aq to -17°—2 With sulphure aced, by dissolving HIO, in hot cone H₂SO₄ and cooling, crystals of 2HIO₃3H₅SO₄ are said to be obtained, the mother liquor deposits other compounds of the .vo acids, if H SO₄2H O is used crystals of 3(H₂SO₂2H₂O) 2HIO₃2H₂O are formed, these compounds are decomposed by water (Millon, J pr 34, 321) Crystalline bodies, supposed to be compounds (Davy), are obtained by mixing cone HIO₃Aq with solutions of H₃PO₄ and HNO₃

Basicity and formula of rodic acid -HIO, is generally looked on as a monobasic acid, analogous to HClO, and HBrO. Besides the normal K salt there exist two acid salts, KHI O. and KH,I,O,, there are no chlorates or bromates similar to these Iodic acid is easily decomposed by heat to water and the anhydride I,O,, such a reaction does not usually occur with monobasic acids Iodic acid is isomorphous with the dibasic The chlorates and acids, succinic and itaconic bromates as a class are easily soluble in water, the iodates are very slightly soluble The ther mal phenomena attending the formation of the three acids, HClO₂, HBrO₃, and HIO₃, mark off HIO, from the two others, thus -

$$\begin{array}{lll} [H,Cl,Aq]=39,320 & [H,Cl,O^3,Aq]=23,940 \\ [H,Br,Aq]=28,380 & [H,Br,O^3,Aq]=12,420 \\ [H,I,Aq]=13,170 & [H,I,O^3,Aq]=55,800 \end{array}$$

The heat of formation of the acid HX decreases as the atomic weight of X increases, whereas in the series of oxyacids the heat of formation decreases from Cl to Br, but then increases very largely from Br to I A similar variation is shown in the K salts, thus—

The lodates are not generally isomorphous with the chlorates and bromates. Thomsen says the only case of isomorphism is presented by the Ba saits. There is no doubt that the constitution of periodic acid is very different

IODATES. 21

from that of perchloric acid, but indic acid shows some fairly marked analogies with periodic Thus, if one molecular proportion of H,IO, (228 grams) is dissolved n 80H,O (1,440 grams), the volume of the solution is 1,440+602= 15002 cc, if the molecular veight of rodio acid is taken as H₂I₂O₆, and this quantity in grams (352) is dissolved in 80H2O, the volume of the solution is 1440 + 599 = 14999 cc other words, one molecular proportion of H,IO,, dissolved in 80 molecular proportions of water, produces the same expansion of the liquid as is produced by one molecular proportion of iodic acid, provided the formula of this acid is tal en to be H2I2Os The foregoing are the chief arguments brought forward by Thomsen for establishing a difference between the constitutions of iodic acid on the one hand and chloric and bromic acids on the other hand, and for showing that nodic and periodic acids are closely related (Th **3, 168, 42**3)

The heats of neutralisation of HClO, HBrO, and HIO, are practically identical (Th When NaOHAq is added to NaIO, a ver, small quantity of heat is developed, about 4 pc of the total heat of neutralisation, but the reaction of NaOH with the monosodium salt of an undoubted dibasic acid is always accompanied by the production of as much, or nearly as much, heat as attends the addition of the first molecular weight c' NaOH to the acid If iodic acid is regarded as dibasic, then the salt $KH_2I_1O_9$ must be looked on as either a compound of the normal salt $K_2I_2O_6$ with $2H_1O_9$ ($2KH_2I_3O_9 = K_2I_3O_6$) or as the acid salt of a hypothetical acid H,I,O,

On the whole there appear to be marked dif ferences between the oxyacids of I and those of The oxyacids of I form more com-Cl and Br plex salts than those of the other halogens The constitution of the iodates and periodates cannot be settled by defining the basicities of the acids HIO, and H₅IO₆ Several series of period ates certainly exist, and there is probably more

than a single series of iodates

The salts KHL₂O₆ and KH₂I₂O₉ may of course be formulated as K₂O 2I₂O₅ H₂O and

K₂O 3I₂O₅ 2H₂O respectively
IODATES These salts are formed by neutraining HIO, by bases, or in some cases by oxidising I in presence of a base (v Iodic acid, Formation, Nos 10 and 11), or by double decom position from the alkali iodates. The iodates are go ierally insoluble or slightly sol in water, the alkalı nodates are readily soluble, KIO, however, is only slightly soluble (S at 20° = c 8) The iodates are decomposed by heat, generally giving a mixture of metallic iodide and oxide, sometimes iodide only Solutions of iodates are more easily reduced than chlorates, reduction of KIO, Aq is brought about by SO, Aq or SH, Aq, with HIAq i dates give I and metallic iodide, with HClAq they give ICl₃, Cl, H₂O, and metallic chloride, dilute H₂SO, produces HIO₃ The following are the chief memoirs on

iodates, they are referred to by numbers in the following descriptions.—(1) Bell, J 1871 298 (2) Berthelot, C R 84, 1408 (3) Cameron, J 1876 284 (4) Clarke, J 1877 48, 267 (5) Connel, S 62, 498 (6) Ditte, C. R 70, 622: (7) Flight, J 1864 147 (8) Gay-Lussac, G. 4.

48, 24, 372, 49, 1, 211 (9) Gorlach, Fr 1869
290 (10) Grosourdy, J Chim méd 9, 428
(11) Henry, B 3, 893 (12) Kammerer, J pr.
79, 94 (13) Kremers, P 84, 271, 97, 5, 99,
443 (14) Ladenburg, A 1.5, 1 (15) Liebig,
P 24, 363 (16) Marignac, J 1856 296.
(17) Melsens, C C 1872 552 (18) Millon,
A Ch [3] 9, 400, 12, 330, 13, 29 (19) Mitscherlich, P 11, 162, 17, 481 (20) Naquet, J.
1860 401 (21) Pellagri, B 8, 1357 (22) Penny,
A 37, 202 (23) Pleischl, S 45, 18 (24) Ram
melsberg, P 44, 545, 46, 159, 62, 416, 90, 12;
115, 564, 125, 147; 134, 368, 499, 137, 305;
(25) Schönbein, J 1857 63 (26) Serullas, P
19, 97, 112, 20, 515 (27) Sonnstadt, J 1872
187 (28) Stas, J 1867 162
Ammonium vodate NH, IO, Lustrous plates,

Ammonium iodate NH, IO₂ Lustrous plates, decompose at 150°, S 26 at 15°, 145 at 100° 8 G 331-334 Formed by action of NH, Aq on I, or of HIO3Aq on NH3Aq or (NH4)2CO3Aq (4, 24, 28)

Barium iodate Ba(IO3)2 H2O By dissolving I or ICl, in BaOAq, or by ppg NaIO, Aq by BaCl₂ or Ba(NO₂) Lustrous monoclinic crystals, which lose H₂O at 130°, and when strongly heated form Ba periodate Ba₂I.O₁₂ S G 5 18-5 28 S 07 at 135°, 15 at 100° (4, 8, 10, 12,

13, 16, 18, 24, 27)

Calcium vodate Ca(IO3)2 Occurs in seawater Formed by adding CaCl Aq to KIO, Aq, or HIO, Aq to Ca(NO,), Aq By action of bleaching powder on KIAq crystallises with 6H.O, and from KIO, Aq + Ca(NO₃) Aq with 4H₂O (Flight) Efflorescent rhombic crystals, on neating gives mixture of CaO and Ca periodate, v insol. water (6, 16, 18, 24, 27)

Copper iodates -1 Cu(IO3)2 2H2O, greenish. blue pp by mixing cone NaIO3Aq and CuSO,Aq, salt with H.O iemains on warming S 33 cold, 65 at 100° -2 3Cu(IO₃)₂3CuO 2H₂O, by action of HIO₃Aq on strongly heated CuO By dissolving (1) in respect to Cu(IO₃)₂ 4NH₄ 3H O is formed (18)

**Cu(IO₃)₂ 4NH₄ 3H O is formed (18)

**Codata Hg(IO₃)₂ By warming NH,Aq

Cu(IO₃)₂ 4NH₄ 3H₂ 0 Is located in Mercury rodate Hg(IO₄)₂. By warming freshly ppd HgO with HIO₅Aq, or adding HIO₄Aq to Hg(NO₃)₂Aq or Hg(C H₁O₂)₂Aq (not HgO₄)₃ to HgCl₂) White powder,

insol water (3)

Potassium vodates -Normal iodate KIO. Prepared by dissolving I in KOHAq, evaporating to dryness, and dissolving out hi by alcohol S G 81, also by passing Cl into I suspended in water, neutralising by KOHAq and evaporating Stas adds 11 pts KClO, to semi fluid KI in a crucible, dissolves, on cooling, in hot water, and recrystallises the KIO, which separates (8, 16, 17, 28) Crystallises in cubical forms SG 18 8 975, KIO Aq SG 1.0741 at 19 5° contains 9 08 KIO, to 100 water (13) S at 5° 5 3, at 9 5° 6 7, at 14° 7 7, at 22 2° 9 2, at 45 8° 16 6, at 69 2° 27 (8) Insol alcohol S G 81 Poisonous Decomposes, at higher temperature than KClO. to KI and O, without production of KIO. heated with MnO₂ forms I, O, and K₂O (8, 24 25) KIO, Aq shaken with finely-divided Fe gives KI (21) From solution in hot dilute H₂SO, Ac rhombic crystals of 2KIO, H₂O separate, which KIO, KHSO, is obtained by heating KIO, it large excess of dilute H₂SO, Aq, evaporating at 25° until KH₂I₂O, crystallises out, and further 22 IODATES

erystallising the mother liquor (16) —2 Diodate or acid codate KHI, O₄ (or K₂O 2I₂O₃ H₂O) Obtained by half neutralising HIO₄Aq by KOHAq; also by acidifying KIO₄Aq by HOl and ppg by alcohol, also by disolving KIO₄ in hot dilute HNO₄Aq (6, 18, 26) Crystallises in three forms, one rhombic and two monoclinic (16) S 133 at 15° (26°) Solution reacts acid Insol alcohol Loses H₄O at 200° (6) Forms a double alt KHI₂O₄ 2KCl, obtained by heating KIO₄ with dilute HClAq, or by adding to ICl₄Aq less than enough KOHAq to saturate it (c ratio KOH 2ICl₂) and allowing to evaporate (16, 24, 26) 3 Tri-lodate KH₄I₃O₅ (or K₂O 3I₂O₅ 2H₂O) Formed by adding a large excess of HIO₄Aq to KIO₄Aq and evaporating, also by heating KIO₅ with large excess of dilute H₂SO₄Aq and evaporating at 25° Large transparent triclinic crystals, lose all H₂O at 200° S 4 at 15° (6, 16, 24, 26) Berthelot (2) describes a basic lodate KIO₅ K₄O obtained by heating KI in O

Silver iodate AgIO, Formed by ppg AgNO₂Aq by HIO₂Aq or NaIO₂Aq Crystallises from NH₂Aq in monoclinic crystals S G 5 4 Soluble without decomposition in dilute HNO₂Aq

(4, 14, 16, 24, 28)

Sodium iodate NaIO, Prepared by saturating 10 pts water holding 1 pt I in suspension, with Cl, neutralising by Na, CO, again passing Cl, again neutralising by Na₂CO, and passing Cl, and so on, finally the solution is evaporated to 110 th its bulk and mixed while warm with half its volume of alcohol, the crystals which separate are pressed and washed with alcohol till free from NaCl (15) Crystallises at under 5° with 2H₂O, above 5° with H₂O, at 70° crystals of NaIO, form, hydrates with 8, 6 and 3 H,O are also described (6, 18, 24) S 2 52 at 0°, 33 9 at 100° (13) Loses O and I when heated (15) According to Rammelsberg (24), a compound of NaI with Na₂O₂ (6NaI Na₂O₃) remains on heating NaIO, With conc HClAq, Cl is evolved, and a compound of HIO, and NaCl remains (6) Double salts with NaI are obtained by evaporating mixtures of NaIO, Aq with NaIAq, NaI NaIO, 8H,O, NaI NaIO, 10H.O. and and **8NaI 2NaIO, 20H₂O are described** (6, 16, 19, 24) The existence of acid iodates is denied (6, 32, ef 18, 22, 26)

Besides the foregoing lodates, the following have been prepared — Cd(IO₃)₂ (24), CO(IO₃)₂ H₂O and Co(IO₃)₂ 6H₂O (4, 24), various Fe lodates (1, 5, 24), Pb(IO₁)₂ (23, 24), Mg(IO₃)₂ 4H₂O (6, 16, 18), Ni(IO₃)₂ H₂O and Ni(IO₃)₂ 6H₂O (4, 24), Sr(IO₂)₂ (24), Zn(IO₃)₂ 2H₂O lodates of Al, Bl, Ce, Cr, Dl, Au, La, Li, Mn, Sr, Sn, U, Y, and Zn also seem to exist, but they have not been fully investi-

gated
PERIODIC ACID and PERIODATES — The only acid which has been isolated is H₁IO₂, but at least five distinct series of periodates are known The anhydride of periodic acid has not been obtained, when the acid is heated it loses H₂O, O, and I, and iodic anhydride, I_{O₃}, remains, Bengieser in 1836 (A 17, 254) stated that by heating periodic acid to 160° it lost water of crystalliss ion, and that O comes off rapidly at 180°, but according to Rammelsberg (J pri-103, 278) and Langlois (J. pr. 56, 36) decomposition begins at c. 130°.

Periodic acid was first prepared by Magnus a Ammermiller (P 28, 514), they prepared it by reacting on AgIO₄ with cold water, whereby the Loid went into solution and another Ag periodate, Ag₄I₂O₂, 8H₂O₃, remained

Formation, -By the action of I on cone HClO₄Aq (Kammerer, P 138, 406, 410)

Preparation -1 Na₂H₃IO₆ is prepared by saturating a hot solution of equal parts NaOH and NaIO, with Cl. concentrating, and allowing to cool (Langlois, A Ch .4, 257) This process yields a mixture of Na,H,IO, and Na,H,IO,, the latter salt is more soluble and may be removed by long continued washing with cold water (Kimmins, C = 51, 357), but it is not necessary to do this in preparing H, O. The Na salt is dissolved in water with addition of just enough HNO, to form a clear solution, and AgNO, Aq is added, a brown pp of Ag.HIO, is thus obtained (Kimmins, C J 51, 358, former observers said that Ag, IO, or Ag, H, IO, 18 produced) brown Ag salt is suspended in water, and shaken with Br, AgBr ppts, and H₅IO₆ along with HBrO, goes into solution, the filtrate is eva porated to the crystallising point, whereby HPrO, is decomposed, and is then placed over H,SO, in vacuo (Kammerer, P 138, 390) -2 Ag HIO, prepared as described in 1 is dissolved in conc HNO₃Aq, and the solution is evaporated at 100°, orange red crystals of AgIO, H,O separate, by treatment with cold water this salt decomposes to H₅IO₆Aq, and Ag₄I₂O₉ 3H₂O which may be again converted into AgIO, by solution in conc HNO₃Aq and evaporation (Magnus a Ammer muller, P 28, 514)—3 Na₃H₃IO₄ prepared as described in 1, and mixed with Na₃H₃IO₄, is dissolved in as little dilute HNO, Aq as possible, Pb(NO,) Aq is added, the pp of Pb periodate (Pb,(IO,), Kimmins) is digested with rather less dilute H,SO,Aq than suffices to decompose it all, and the liquid is filtered and evaporated (Ben gleser, A 17, 254)

Properties — H, IO, crystallises in transparent, colourless prisms, probably monoclinic (Rammels berg) MP 133° (Rammelsberg, J pr 103, 278), 130° (Langlois, J pr 56, 36), melting is accompanied by partial decomposition (Bengieser, A 17, 254, put the temperature of decomposition at 180°) H, IO, does not lose weight at 100°, nor by keeping over H₂SO, Very deliquescent; fairly sol in alcohol, slightly sol in ether. Thomsen (B 7, 71, Th 2, 427) gives the following data for S G and expansion of H, IO, Aq —

Ratio of H ₄ IO ₄ H ₄ O	SG of solution	Expansion for each formula-weight of acid
H,10, 20H,0	1 4008	59 77
,, 40 ,,	1 2165	59 30
, 80 ,,	1 1121	59 9 9
n 160 n	1 0570	6 0 2
,, 820 ,,	1 0288	60 0

The volume when aH,O is present is expressed by the formula Va=18a+596 The following thermal data are taken from Thomsen (Th 2, 166) —[H³,I,O⁴]=185,780, [H³IO⁴,Aq]=-1880, [I⁴,O,Aq]=27,000 H,IO₄Aq exposed to air becomes yellow, and smells strongly of bzone

Reactions —H.IO.Aq reacts as an energetic oridiser, with HÖl it gives Cl and HIO. (M a. A., Lo), with P and Bi it forms P.O. and Bi.O.

Kämmerer, i.e); C₂H₄O₂, C₂H₂O₄, and many other Cacids are oxid sed to CO₂, SO₂Aq, SH₂, and HI are also oxidised, with Zn, Fe, Hg, and Cu t forms ZnO, Fe,O4, HgO, and Cu(IO2)2 respec

Periodates Most of the peri dates are in soluble in water, they are generally prepared from the Na or K salts by double decomposition from solutions acidified with HNO. Many of them are decomposed by heat giving O and metallic iodides eg KlO4, AgIO4, others evolve O and I, and leave either oxide, eg salts of Ni and Mg, or a mixture of oxide and iodide, g salts of Pb, Cu, Cd Hg salts give iodide and Hg, NH, salts decompose explosively to I, N, O, and H,O Very many periodates are known, they may be divided into several classes, the following sche ie presents the chief classes and the chief salts in each class The nomenclature is that adopted in Gmelin Kraut's Handbuch All the acids except H, IO, are hypothetical, formulæ of salts are given here without water of cry stallisation -

Ba₃(IO₄)₂ is obtained, and Ca(IO₃)₂ undergoes a similar reaction The salts obtained by double decomposition from alkali salts of the orthoseries, c. of the dimeso- series, usually belong either to the ortho- or mesc series, thus the following salts are obtained -

Starting from Na,H,IO. Starting from K,I,O. Cu2HIO4 Cu HIO. FeH,10. Fe,(IO,) ortho Pb,H,(IO,)2 Pb,H,(ĬŌ,), (Ag₂H,ÌO Ag₂H,IO₄ CdHIO. CdHIO, Ag,HIO, meso Ag.HIO. N1,(IO,)2)

When a salt is obtained by ppn from an acidified solution of an alkali salt, the series to which the ppd salt belongs is conditioned by the relative quantity of soid present, thus when AgNO, is added to a solution of Na,H,IO, k,I.O. or KIO, acidified by a little HNO. Ag, HIO, is obtained, when more HNO, is present the pp is Ag.H.IO., and when conc acid is pre-

Periodates.

A P RIODAL LOS					
Ortho-periodates derived from H _s 10 _s	Meso periodates derived from H 10 _s (H _a 10 -H _a 0 -H 10 _s)	Immeso-periodates derived from $H_aI_aO_a$ $(2H_aIO_a-3H_aO=H_aI_aO_a)$	Meta-periodates derived from HIO, (H,10,-2H,0=HIO,)		
Ba _s (IO _s),	Ba ₁ (IO ₂) ₂	Ba I ₂ O ₆	$Ba(IO_4)_2$		
BeH IO.	Cd,(IO),	Cd.I.O.	Cd(IO ₄) ₁		
Ca (IO),	CqHIO,	Ca ₂ I O _•	Ca(IO),		
Cu,HIO,	$Pb_{s}(IO_{s})_{s}$	Cu,I,O,	$Fe(IO_4)_2$		
Fe (IO,),	Ni,(10,),	FeHIO,	Pb(IO),		
FeH,IO.	k,IO,	Mg I O	KIO,		
Hg,IO.	Ag HIO,	N.J.O.	AgIO,		
Ag IO.	$Sr_{s}(1O_{s})_{2}$	K,I.O,	NaIO,		
Ag H,IO.		K _i HI O,	Sr(IO),		
Ag H ₂ IO ₄		Ag.I.O.			
Na H ₃ IO ₄		Na.I.O.			
Na H ₂ IO ₄		Sr I ₂ O ₄			
$Sr_s(IO)_s$		$\operatorname{Zn}\ \operatorname{I}_{z}\operatorname{O}_{\bullet}$			
Zn _s (IO _o) _r .					
Di peri dates		Dimeso-diversalates	Trimeso periodates		
derived from H 1,0,		derived from H ₁₀ 1 O ₁₀ (2H ₀ I ₁ O ₁₁ - 3H ₀ O = H ₁₀ I ₂ O ₁₀)	derived from H ₁₀ I ₀ O _m (6H ₂ IO ₀ -10H ₂ O=H ₁₀ I ₀ O _m)		
(2H,10 ~H,0 = H,1,0	.)				
$Cd_1I_2O_{11}$		Ba _s I ₄ O ₁₉	Ba,I,O,		
Cu,I On		$\Delta g_{10}I_4O_{10}$	Sr _s I _s O _{ss}		
$Mg_{i}l_{i}O_{i1}$					
$Hg_{i}I_{i}O_{i1}$					
$\mathbf{A}\mathbf{g}_{\mathbf{a}}\mathbf{I}$ $\mathbf{O}_{\mathbf{n}}$					
$\mathbf{Zn_4IO_{01}}$					

The series to which a periodite belongs seems to depend partly on the nature of the base, and to a large extent on the conditions of preparation By neutralising H,IO,Aq by NaOHAq Rammelsberg (P 134, 368, 499) ob tained NaIO, , by neutralising the same acid by various carbonates the following salts have been obtained

By passing Cl into a hot mixture of KIO, and KOH, KIO,, K,I,O,, and K,HLO, are produced, but the Na salts formed under similar conditions

sent the salt AgIO, is obtained Boiling salts of the ortho, meso, or dimeso series with HNO, Aq as a rule produces salts of the meta series Acid salts of the ortho series are changed to normal salts of the meso or dimeso- series by heating, and acid salts of the meso series are changed to normal salts of the dimeso series, thus Pb,H,(IO,), at 275° gives Pb,(IO,), and H.O, and Ag,HIO, gives Ag.I.O. and H.O at 300° Some of the periodates show very distinctly the difference between so called 'water of crystallisation' and 'water of constitution', thus Ag,HIO, (which might be written Ag,I,H,O,e) and Ag,I,O,H,O (which also might be written Ag,I,H,O,e) are quite different bodies, the change 2Ag,HIO,=Ag,I,O,+H,O occurs at 300°, but Ag.I.O, H.O loses H.O at 130°, again Ag.H.1O. (which might be written are Na,H,IO, Na,H,IO, Na,II,O, and pe Ag,I,H,O,;) is a dark red pp, obtained by alding haps NaIO, By heating Ba(IO,), the salt AgNO, to Na,H,IO, in a slight excess of HNO,Aq, whereas Ag, I2O, 3H2O (which also might be written $Ag_4I_2H_8O_{12}$) forms light yellow crystals, and is obtained by treating $AgIO_4H_2O$ with water As a rule water of crystallisation is removed at 100°, thereas the temperature of acid salts must be raised to 270°-300° before change begins with evolution of water (For a comparison of the classes of periodates, v Kimmins, C J 55, 152) Thomsen (Th 1, 244) has determined the heat of neutralisation by KOH of Halo, with the following results .-

" 1	[H°10°Aq, n KOHAq	d(f
•	•	21,440
2	2 6,590	8,150
8	29,740	2,800
5	32,0 40	-,

From these results Thomsen concludes that H,IO, is dibasic, but that basic salts are produced when more than 2KOH reacts plain the existence of many of the periodates, Thomsen prefers to double the formula of the acid and to represent it as normally tetrabasic, thus H₄I₂O₉.3H₂O. he classifies the chief periodates as follows

> Normal salts R140, 3H20 Basic salts (1) R¹¹, L₂O₁₀ 2H₂O (2) R¹¹, L₂O₁₁ H₂O (3) RII, I,O,,

The existence of undoubted acid salts, s.e salts in which the H is not combined with O in the form of H2O, militates against the classification of Thomsen The reaction of KOHAq with H.IO.Aq is almost certainly a complex occurrence

In the following description of periodates only one or two salts in each series are described ın detail

The following are the principal memoirs on periodates, they are referred to in the following paragraphs by numbers (1) Atterberg, J 1873 257, (2) Bengieser, A 17, 250, (3) Blomstrand, B 3, 317, (4) Fernlund, J 1867 165, (5) Groth, P 134, 536, (6) Kimmins, C J 51, 356, 55, 148, (7) Langlois, J 1852 345, (8) Lautsch, J pr 100, 65, (9) Magnus a Ammermuller, P 28, 514, (10) Philipp, B 3, 4, (11) Rammelsberg, P 44,545, 46, 159, 62,416, 90,12, 115,584, 125,147, 184, 368, 499, 137, 305, (12) Ritter, Gm -K (6th ed), 1 [2] 303

Ortho-series, salts derived from H,IO, Barum orthopervolate $Ba_s(IO_s)_s$. Prepared by heating $Ba(IO_s)_s$ in a current of dry air (Sigiura a Cross, C J 85, 118), by passing I vapour and dry air over heated BaO (S a C), by heating Bal, in a current of dry air so long as I is given off (S a C) Insol water, sol

HNO₃Aq, heated in H gives BaI, and BaO
Silver orthoperiodates—1 Ag₃IO₆ said to
be ppd as a brown salt by adding AgNO₃Aq to a neutral solution of an alkaline periodate, also by shaking Ag₄I₂O₆ 3H₂O with cold AgNO₂Aq (11), Kimmins (6) failed to obtain this salt, sol in HNO,Aq and in NH,Aq -2 Ag,H,IO, dark red pp by adding AgNO,Aq to Na,H,IO,Aq or K.I.O.Aq in slight excess of HNO. (6) -

8 $Ag_2H_2IO_4$, slate coloured pp by adding $AgNO_3Aq$ to $Na_1H_3IO_4Aq$ or $K_4I_4O_4Aq$ in presence

of a fair amount of HNO, (6)

Sodium or thoper odates Na,H,IO, Na, H, IO, , white granular pps , formed by passing Cl into a bo ing solution of equal weights of NaIO, and NaOH, the second salt is less soluble than the first, from which it may be sepa rated by long continued washing with small quantities of cold water (b)

For descriptions of the other salts of this series v (1) for Be salt, (6) for Cu and Fe salts, (8) for Hg salt, (11) for Ca, Sr, and Zn salts (for for

mulm of salts, v p 23)

Meso series, salts derived from hypo thetical H,IO,

ppg the corresponding K salt by Ba2NO₁Aq (11)

Potassium mesoperiodate K, IO, 4H,O KiO, is prepared by saturating with Cl a hot cond solution of equal weights of KIO, and KOH, and repeatedly crystallising, the salt is dissolved in water and the solution is ppd by alcohol (11)

Silver mesoperiodate (acid salt) Ag TIO, A dark brown pp by ppg Na₂H₁IO or K₁I₂O₃ in just enough dilute HNO₃Aq to form a solution

For description of other salts of this series (formulæ given on p 23), v (6) for salts of Pb and Ni, and (1") for salts of Cd (crystallises with 5H2O) and Sr

Dimeso series, salts derived from hypo

thetical H.I.O.

Barrum dimesoperiodate Ba,I,O, Obtained by ppn from alkali periodates in presence of HNO, By neutralising H₃IO,Aq by BaO \(\frac{1}{3}\), a salt with 7H2O is obtained, which loses 4H2O at 100°, and on strongly heating goes to Ba IO. (11, 7, 8)

Ferric dimesoperiodate (acid salt) Italiao. By ppg solution of Na.H. IO. or K.I.O. by FeCl.Aq and drying at 100° Boiling with Boiling with dilute HNO, Aq does not change this salt (6)

Potassium dimesoperiodates K.I.O. and K.HI.O. Both salts are obtained by passing Cl into KIO₃ mixed with KOHAq (6) If equal weights of the KIO, and KOH are used, and the KIO, which separates is removed by filtration, the filtrate on concentration gives K, I,O,, if this filtrate is exactly neutralised by HNO, the ilt $K_4I_2O_9$ 3H O (v also 11) crystallises out without concentration, if excess of HNO₂ is u ed, $K_3HI_2O_9$ is obtained A solution of I IO, to which KOH is added is said to give triclinic crys tals of K₁I₂O₂ 9H₂O on concentration (5, 9) K₄I₂O₆ is soluble in KOHAq, S 10 3 cold water, solution has alkaline reaction, Cl led into boil ing K₄I₂O₂Aq produces KIO₄, with I, KI and KIO₃ are produced strongly heated leaves 2KI K₂O (11)

Silver dimesoperiodate Ag, I,O, 3H2O Light yellow crystals, obtained by treating AgIO, H.O. with cold water (6, 9) Heated to 100° for 12 hours claret coloured crystals of Ag, I2O, H2O are formed, and when the temperature is raised to 130° and kept there for many hours a chocolate coloured powder, Ag,I₂O₉, remains (6) When Ag,I₂O_q is seested with NH₂, q, Ag,I₂O₁₁ is pro

&uced (11)

For descriptions of other salts of this series

(formulæ given on p 28\ v (2) for salt of Ca (crystallises with 7 and 9 H₂O), (6) for salts of Ni and Zn, (7) for Sr salt (crystallises with 3H₂O), (8) and (9) for Na salt (c-ystallises with 3H2O), and (11) for salts of Cd (crystallises with 9H₂O), Cu (with 6H₂O), Mg (with 1 and 15 H₂O)

series, salts derived from hypo Meta

thetical HIO,

Ferric metaperiodete Fe(IO,). Bright yel low, produced by boiling FeHI,O, for some time with conc HNO, Aq (6)

Potassium metaperiodate KIO, Prepared by saturating with Cl a boiling cone solution of equal parts KIO, and KOH, cooling, and crys tallising repeatedly from water (6, 7, 9, 11) S 35 cold we er, almo 'rsol KOHAq KIO,Aq shows acid reaction At 300° forms KIO,, de composed by I at 160° Reduced in solution by kI to KIO, and I, which is then oxidised to KIO, (8, 9, 10)

Silver metaperiodate AgIO, By dissolving Na₂H₃IO₄ or Na₃H IO₄ or K₄I₂O₅ in cone HNO₃Aq and adding AgNO₃, also by treating Ag,H₃IO₆, Ag₃H₃IO₆, or Ag,I₂O₆ with conc HNO₃Aq and evaporating on steam bath Orange coloured Ciystals are AgIO, H2O, heated to crystals 130 for 6 hours AgIO, remains as a bright yellow powder (6) Decomposed by water giving Ag, LO, 3H,O (11)

For descriptions of other salts of this series (formulæ given on p 23) v (11) for salts of Ba, Cd, Ca, and Sr (crystallises with 6H2O), (5), (7), (3), (9), and (11) for salt of Na (crystallises with

2 and 3 H.O)

Di series, salts derived from hypothetical H_aI₂O₁₁

Cadmium diperiodate Cd_I_O_1 3H2O ppg a slightly acidified solution of NaIO, by a coluble Cd salt (11)

Silver diperiodate Ag, LO11 By treating $Ag_1I_2O_0$ with NH_1Aq (8, 11)

For descriptions of the other salts of this series (formulæ given on p 23) t (11) for salt of Cu (crystallises with H O and 7H₂O), (11) for salt of Mg (with 6 and 9 HO), (11) for salt of Hg (cf 8), (7) for salt of Zn (cf 11)

Dimeso di and Tri meso series, salts derived from hypothetical H1. I.O1., and H1. I.O2.

respectively, v (8) and (11)

Iodine, phosphides of, better called Phos phorus wodules, v Phosphorus

Iodine, selenides of, better called Selenion todides, v Selenion

Iodine, silicides of, better called Silicon wodides, v Silicon

Iodine, sulphides of, better called Sulphur todides, v SULPHUR

Iodine, tellurides of, better called Tellurium MMPM

iododes, v Tellurium M 10D0 ACETIC ACID C2H2IO2 s.c. CH_I CO_H '(ol w 186 [82°].

Formation -1 By digesting bromo acetic other with KI and alcohol, for about two hours in the dark, distilling off the resulting iodoacetic ether and decomposing it with baryta-water (Perkin a Duppa, P M [4] 18, 54) -2 By boiling Ac₂O with iodine and iodic acid (Schützenberger, J. pr. 107, 108) -38. By the exidation of iodo-acetic aldehyde (Chautard, A Ch [6] 16, 152)

Properties - Trimetric plates, decomposed by heat

Reactions —1 Moist silver oxide yields glycollic acid -2 Resolved by HI, even in the cold, into acetic acid and free iodine (Kekulé, $C \ J \ 17, 207$)

Salts The NH, and K salts are very soluble, orystalline, and non deliquescent.—BaA'₂ crystalline, m sol water, ppd from aqueous solution by alcohol—PbA'₂ prisms In solution it easily splits up into PbI, and glycollic acid

Methylether MeA' (170°) Pungent liquid (Aronstein & Kramps, B 14, 604)

Ethyl ether EtA' (180°) From scetic ether, KI, and alcohol (P a D) From bromofrom chloro acetic acid, KI, and alcohol (96 p c) by heating on the water bath in the dark Easily obtained by heating chloro acetic ether with Cal, 3 aq at 75° (Spindler, A 231, 272) Pungent heavy oil Decomposed by LtI at 230° giving acetic ether and ethylene iolide (Aronstein a Kramps, B 13, 489, 14, 604) With Me,S it forms MeS CH, CO,H and, finally, S(CH,CO,H).

Chloro ethyl cther CI CH, CH, O CO CH I SG 10 1954 chloro ethyl chloro acetate by gently heating with an alcoholic solution of NaI (Henry, C R 97, 1308) Very pungent oil Turns brown in

davlight

Propyl ether Pra' (198°) 8 G I 1 679 From propyl chloro acetate and alcoholic NaI

(Henry, C R 100, 114) Pungent oil

Amide CH I CO NH, [158°] Formed from methyl rodo acctate and alcoholic NH, (Henry Also from chloro acetamide and alcoholic KI, by standing a few days in the cold (Menschutkin a Jermolajeff, Z 1871, 5) Small needles or prisms

Nutrule CH, I CN Iodo acetonitrile (187º) S G 12 2 307 I iom chloro acetonitrile and alcoholio NaI (Henry, C R 103, 413) Colourless, very pungent oil, which becomes brown in daylight V sol alcohol and ether Slightly decomposed on distillation, with liberation of some lodine and HCy AgOAc forms CH (OAc) CN

Di 10do acetic acid CHL.CO.H Formed by heating di bromo acetic ether with KI, converting the resulting di iodo acetic ether into a Ca salt with milk of lime, and adding HCl (Perkin a. Duppa, C J 13, 1) Crystalline sulphur yellow compound, volatile in the cold, sl sol water Does not blister the skin The K and Na salts are deliquescent—BaA', trimetric crystals, giving off iodine when heated—CaA', silky yellow needles - PbA', crystalline pp - AgA' yellow crystalline powder

Ethyl ether EtA' Formed by treating di chloro acetic ether with Cal, 3 aq at 75° (Spindler, A 231, 273) Formed also by adding iodine to a solution of diazo acetic ether in ether (Curtius, J pr [2] 38, 433) Oil, volatile with

steam, reddens on exposure to air

Amide CHL CONH, [202°] Formed by the action of rodine upon a cold alcoholic solution of diazo acetamide (Curtius, B 18, 1285) Formed also by the action of conc NH, Aq upon di-iodo-acetic ether Greenish-white prisms (from hot water), v sl sol. water. Very stable towards acids and alkalis.

IODO ACETIC ALDEHYDE CH,I CHO S G

Formation -1 By boiling an aqueous solution of chloro acetic aldehyde with KI, allowing to stand for 12 hours, and then extracting with ether (Glinsky, Z [2] 4, 618) -2 By the oxida tion of a solution of iodine in alcohol

Preparation -By mixing iodine (50 g), iodic acid (20 g), aldehyde (30 cc) and water (60 cc) and leaving the closed flask to stand for about a week (in summer) Water (500 cc) is then added, when the 10do acetic aldehyde separates as an oil (Chautard, A Ch [6] 16, 145, C R 102, 118, C N 54, 87, cf W P Bloxam a E F Herroun, C N 53, 301, 54, 133)

Properties -Limpid colourless oil, unin flammable Blacken's rapidly when exposed to Its vapour is excessively irritating Cannot be distilled even in vacuo Decomposes at 80° Miscible with alcohol, ether, chloroform, and CS₂ Sl sol water Forms a crystalline Forms a crystalline compound with hydrate

NaHSO,

Reactions -- 1 Dilute aqueous KOH forms iodoform Conc KOHAq resinifies it -2 Am monta either aqueous or alcoholic forms ammo nium iodide and various bases, e.g. oxytiialdine (O2H3)2N C2H,OH -3 Chlorine and bromine at ordinary temperatures displace iodine giving chloro and bromo acetic aldehydes and resins 4 All mineral acids decompose 10do acetic aldehyde - 5 Reducing agents (Na amalgam, Zn and HCl) remove the iodine -6 Oxidation with have yields CH2I CO2H [82°] -7 NaOLt and KOEt yield only resinous matters -8 Silver acetate yields acetic ether (74°) —9 AgCN gives CH₂(CN) CO H —10 AgSCN similarly gives CH2(SCN) COH -11 The amines form crystal line bases with elimination of water Thus amiline gives CH₂I CH(NH C₂H₃),, and p tolu idine gives CH I CH (NH C,H, CH,)

Tri-iodo acetic aldehyde CI, CHO (above 200°) From chloral or bromal and HI (Bertrand, J 1881, 588)

IODO-ACETO ACETIC ETHER

CH, CO CHI CO₂Et SG 14/14 1 7053 From cupric aceto acetic ether and iodine in ether (Schönbrodt, A 253, 178) Yellowish oil, v sol ether Begins to decompose at 25° AgCl gives chloro aceto acetic ether AgCy gives di oxy-terephthalic ether dihydride AgNO₂ forms nitro aceto acetic ether Reduced silver gives di acetyl-fumaric ether Sodium aceto acetic ether in benzene forms di acetyl succinic ether

IODO ACETONE C.H., IO ic CH., CO CH., I S.G. 12 217 Formed by the action of KI on chloro-acetone (Glutz a E Fischer, J pr [2] 4, Prepared by mixing acetone (200 cc) with iodine (100 g) and iodic acid (10 g), and, after a week, boiling for three hours, adding water (500 cc), drying the separated oil over CaCl, and distilling in vacuo in the dark (De Clermont a Chautard, C R 100, 745) pungent oil Not inflammable Decomposes slowly in sunlight, but more rapidly when heated Reduces Fehling's solution Mineral acids con vert it into CH, I CO CH, I Silver chloride forms, chloro acetone LOAc gives CH, CO CH, OAc

Di iodo-acetone C.H.I.O 10 CH.I CO CH.I (62°) (M Simpson, J. pr 102, 880, O Völker,

4 192, 90).

Formation -1 From acetone (48 g), water (1000 g), and ICl₂ (96 g) a* 68° As soon as reaction begins the liquid is cooled The oil that separates is exposed to the air till crystals separate (eight weeks), these are recrystallised from alcohol -2 Trom CH,Cl CO CH,Cl and aqueous

Properties - White needles Violently attacks the mucous membrane Decomposed when heated Not very soluble in chloroform, CS2, or Sol benzene, v sol ether and acetone Cannot be distilled undecomposed

Reactions—1 Silver chloride gives solid CH Ol CO CH Cl [43°]—2 Decomposed by cold KOH, and by boiling K₂CO₃—3 Not converted into acrolein or acrylic and by Ag₂O, AgCy, or HgO -4 Hg.I. forms acetone, todc acetone, HI, and acetic acid, but no acroleir -5 Zinc and acetu acid reduce it to acctone

p IODO ACETOPHENONE

[14]C H,I CO CH, [79°] Obtained by diazotising p amido acetophenone, and heating the diazochloride with excess of HI (Klingel, B 18, 2692) White flat needles or plates Easily sol alcohol and ether, and to a certain extent in hot - ater By CrO, it is easily exidised to p iodo benzoic acid [266°]

IODO-ACETOTHIENONE V IODO THIENYL METHAL KETONE

10D0 ACETYLENE HC CI Formed by passing a current of steam through a solution of barium iodopropargylate (CICO) Ba (Baeyer, B 18, 2274) Crystalline solid Sol water Vola tile with steam Very poisonous It gives a purple red pp with ammoniacal CuiCl2, which is soon converted by an excess of the copper solution into copper acetylene and cuprous iodide It soon polymerises on keeping

D1 10do acetylene IC CI [78°] Formed by the action of iodine upon acetylene silver By treatment with an excess of ammoniacal Cu Cl. it is converted into copper acetylene and cuprous iodide It readily polymerises (Baeyer, B 18,

Di 10do diacetylene IC C C CI [101°] Co lourless crystals Odour resembling 10doform Formed by the action of a solution of iodine in aqueous KI upon silver diacetylene By treat ment with an excess of ammoniacal Cu₂Cl₂ it yields copper diacetylene and cuprous iodide It explodes violently on heating, with a brilliant red flash It soon polymerises on keeping (Baeyer, B 18, 2276)

IODO ACETYLENE CARBOXYLIC ACID .

IODO PROPIOLIC ACID

IODO ACIDS v IODO COMPOUNDS

IODO ACRYLIC ACID C,H,I CO,H Large, colourless, four sided prisms [65°], or plates Easily soluble in water, alcohol, and ether Formed by the addition of HI to propiolic acid (Bandrowski, B 15, 2703, Stolz, \hat{B} 19, 542) The Pb and Ag salts are white crystalline

as Di iodo-acrylic acid CHI CI CO.H [106°]. Formed by treating propiolic acid with an ethereal solution of rodine (Homolka a Stolz, B 18, 2284) Colourless prisms, or long needles Volstile with steam Easily soluble in alcohol, ether, and hot water

β Di iodo-acrylic soid I_cC CH CO_cH [133°]. Formed by addition of HI to rodo proprolic acid ICiC CO.H (Homolka a Stolz, B 18, 2284) Prisms Easily soluble in alcohol and ether, tolerably in hot water, very sparingly in cold

Not volatile with steam

Tri-iodo-acrylic acid CI, CI CO2H [207°] Formed by the action of an etherea, solution of iodine upon iodo-propiolic acid CI C CO,H (Ho molka a Stolz, B 18, 2286) Large colourless prisms Easily soluble in alcohol and ether, insoluble in cold water

IODO-DI ALLYL-ACETIC ACID C.H.11102 te CI(C,H_s), CO₂H Iodo octinoic acid From C(OH)(C,H), CO₂H and fuming HIAq (Schat zky, J R 17, 78) Crystals, insol water, v sol From alcohol and other Easily decomposes

IODO ALLYL ALCO.YOL C.H.I OH [160°] Produced by the action of aqueous Na, CO, on di iodo propyl alco ol (Hübner a Lellmann, B 18, Highly volatile with steam 460) Needles Insol water, sol alcohol, chloroform, and HOAc

No attacked by Ac,C

IODO ALLYLENE C.H.I te CH. C CI (?) (98°) SG 17 From silver allylene and iodine in KIAq (Liebermann, A 135, 270) Pungent oil Almost insol alcohol With zinc and HCl it gives off allylene Combines with iodine (1 mol)

Iodó allylene CH, I C CH Propargyl woulde (115°) S (r 2 20177 From propargyl bromide and alcoholic NaI (Henry, B 17, 1132) Liquid V e sol alcohol and ether, m sol coiling water Readily combines with iodine, forming colourless needles of CHI CI CH₂I [41°] Combines with mercury

IODO ALLYLENE IODIDE v TRI-IODO PRO-

TRI-IODO-ALLYL ETHYL OXIDE C.H I,O t.e CI, CI CH, OEt From the silver derivative of propargyl ethyl oxide and iodine in ethereal solution (Liebermann, A 135, 285) Oil

DI IODO ALLYL IODIDE v TRI IODO PRO

TETRA-IODO-DI-ALLYL PHOSPHITE

(CHI CI CH₂O)₂P(OH) [49°] From propargyl alcohol, todine, and red phosphorus (Henry, B 8, 398, 17, 1133) Long slender needles (from alcohol) Very pungent

IODO-AMIDO-BENZOIC ACID C H, INO. 1 c C.H. I(NH2)CO2H [3 20r6 1] [1370] Formed by reducing iodo nitro benzoic acid [235°] dissolved in glacial acetic acid (Grothe, J pr [2] 18, 326)

Dark brown crystals V sol water By further reduction it forms o amido benzoic acid [148°] -

HA'HCl — BaA'₂ aq Iodo amido-benzoic acid C₂H₃I(NH₂)CO₂H [209°] From 10do nitro benzoia f8 6or2 11" acid [174°] Needles, al soi water May be reduced to o-amido benzoio acid -- CaA', 2aq --

SrA'₂ --BaA'₂.
Di-iodo-m amido bensoic acid

C.H.I.(NH.)CO.M Formed, together with N.(C.H.I.CO.H), by treating an alcoholic solu tion of m amido benzoic acid [173°] with iodine and mercuric oxide (Benedikt, B 8, 384) acids are separated by fractional ppn of their alcoholic solution by lead acotate. Long needles Decomposed by heat Insol water, v sol alcohol, ether, aqueous acids, alkalis, and Na,CO, -KA' long silky needles, obtained by mixing alcoholic solutions of the said and KOH.

Di-iodo-p amido-benzoic acid C₀H₂I₂(NH₂) CO₂H [above 300°] Obtained by dissolving p amido benzoic acid in dilute HCl and passing in the vapour of ICl (2 mols) (Michael a Norton, Am 1, 264) Tables Insol water, alcohol, and HOAc, sol nitro-be izene Does not combine with acids -NaA' 5aq long white needles, sol hot water.—BaA', 4aq needles, sol hot water -AgA'

DI IODO-p AMIDO PHENOL

C_eH₂I₂(NH₂)ÔH [222°] Formed by reducing the corresponding nitro phenol with SnCl, and HCl (R Seifert, J pr [2] 28, 437) Needles (from alcohol) or plates (from MeOH) With HCl and bleaching powder it gives di-lodo quinone chlorimide $(q \ v)$ With H SO, and K,Cr,O, gives di lodo quinone $(q \ v)$ —B'HCl Decomposed by water

IODO AMIDO THYMOL

C.HIMePr(OH)(NH) [6 5 2 1 4] From the oxim of 10do thymoquinone by reduction with SnCl, (kehrmann, J pr [2] 39, 392) Its stanno chloride forms large colourless prisms

IODO AMIDO-TOLUENE SULPHONIC ACID C₆H₂MeI(NH₂) SO₃H [1 4 2 5] Formed from the corresponding nitro toluidine sulphonic acid by diazotisation and treatment of the product with cone HIAq at 135° (Foth, A 230, 308) Slender silky needles (from water) V sl sol cold water

IODO AMYL ALCOHOL C, H, IO? Amylene glycol wodhydrin Formed by shaking un amylene with iodine, water, and HgO (Lippmann, Z 1867, 17, 4 Suppl 5, 124) Heavy oil, decomposed by distillation

IODO AMYLIDENE ANILINE

C,H,I CH \C,H, Formed by heating iodo iso valeric aldehyde with aniline (Chautard, A Ch [6] 16, 168) Yellow prismatic needles or rect angular tables Decomposed by heat V sol alcohol, sol water and other, v sl sol benzene and chloroform With HCl it forms an uncrystallisable salt

o IODO ANILINE C.H.IN te C.H.I(NH2) [1 2] Mol w 219 [56 5°] Formed by heating at 100° a mixture of o iodo nitro benzene (25 pts) with ferrous sulphate (250 pts) and a moderate excess of dilute ammonia. The product 18 extracted with ether, the extract distilled with sterm, the product dissolved in dilute H.SO. freed from 10do nitro benzene by shaking with ether, ppd by ammonia and the iodo aniline again distilled with steam (Korner a Wender, (, 17, 486) Long silky needles, with an odour resembling pyridine Sl sol hot water, v sol other solvents Exhibits an alkaline reaction. Turns brown on exposure to air and light Decomposes when heated, evolving iodine converts it into di-iodo aniline [96°]

Salts-B'HClaq small prisms or cubes, turning opaque on exposure, with loss of water of crystallisation —B'₁(H₂SO₄)₂ silky needles, m sol water —Nitrate small four sided tables.

Acetyl dersvative C.H.I NHAc [110°] Prisms or hexagonal tables, m sol hot water, wasol alcohol

m-Iodo-aniline C.H.I(NH2) [1 3] [27°] Formed by reducing m iodo nitro-benzems (Griess, Z 1866, 218) Silvery plates Acetyl derivative C.H.I(NHAc) [119 5]

Glistening needles; more stable than the o-isomeride (Körner a Wender, G 17, 486)

p-Iodo-aniline C.H.I(NH2) [14] 763°1 Formed by reducing p iodo-nitro-benzene [172°] (Griess, C J 20, 85) Formed also by adding iodine (3 pts) to aniline (2 pts) and mixing the solution with aqueous HCl (S G 111) when piodo aniline hy trochloride is ppd (Hofmann, A 67, 64) Prisms or needles, heavier than water Has no action on litmus SI sol cold water, v sol other solvents Bromine converts it into tri-bromo-aniline — B'HCl thin laminæ or needles (from hot water), sl sol cold water, almost insol HClAq, sol alcohol, insol ether -B'2H2PtCl, orange pp --B'2H2C2O, long needles, sl sol water and alcohol, insol ether -B'2H2SO4

Acetyl derivative C_eH₄I(NHAc) [183°] S (alcohol of 95 p c) 6 4 at 20 5° Small glistening tables or trimetric prisms (K & W) Formed by dissolving acetanilide in glacial acetic acid, and passing in vapour of iodine chloride, the yield being 85 pc (Michael a Norton, Am 1, 255)

Bensoyl derivative CaH, INHBz [180°] Long needles (Hubner, B 10, 1717) An 180 meride [210°] is formed from benzanilide and

Di iodo aniline C₆H₂I₂NH₂ [4 2 1] Formed by the action of iodine on phenylated white precipitate' NHPh HgCl (Rudolph, B 11, 78) Formed also by passing ICl (2 mols) into ___ ation of aniline in HOAc (Michael a Norton, Am 1, 255, B 11, 109) Needles Sl sol boiling water and ligroin, v sol ether, chloroform, CS2, acetic ether, and hot alcohol Volatile with steam It is slightly basic, but its hydrochloride is decomposed by cold water -B'HCl: long white needles, decomposed at 50°. — B'₂H₁PtCl₂—B'HNO₃—B'₂(H₂SO₄)₂

Benzoyl derivative C.H.I.NHBz [181°]

Slender needles (Rudolph)

Tri - iodo - anılıne $C_6H_2I_3(NH_2)$ [6 4 2 1] [185 5°] Prepared by the action of ICl (3 mols) on a solution of aniline in HClAq (Michael a Norton, Am 1, 255) Long white needles, sol CS₂ and acetic ether, insol water

IODO-ANISIC ACID v Methyl derivative of

IODO OXY-BENZOIO ACID

IODO-BENZENE C.H.I. Phenyl wodide Mol w 204 (188°) S G $\frac{2}{8}$ 1 8606, $\frac{152}{9}$ 1 8380 (Young, C J 55, 486), $\frac{9}{4}$ 1 8578, $\frac{19}{4}$ 1 8403, $\frac{19}{4}$ 1 8321 $\frac{19}{4}$ V 130 55 (R Schiff, $\frac{19}{4}$ 19, 564) $\frac{19}{4}$ = 1 6189 (Seubert, $\frac{19}{4}$ 22, 2520).

Formation - 1 By treating phenol with iodine and phosphorus The yield is bad (Williamson a Scrugham, C J 13, 244) -2 By the action of ICl on sodium benzoate (Schutzenberger, C. R 52, 963) -3 By heating benzene for some time with iodic acid (Peltzer, A 186. 194) -4 By the action of HI on diszobenzene salts (Griess, J 1866, 447) — 5 By heating benzene (20 g) with iodine (15 g) and iodic acid (10 g, at 220° (Kekulé, A 137, 157)—6 From benzene, rodine and FeCl, (Lothar Meyer, A 281, 195) -7 By the action of excess of iodina on phenyl hydrazine (E v Meyer, J. pr. [2] 86,

Preparation -By allowing chloride of iodine to drop slowly into a large excess of bensene

containing a small quantity of aluminium chloride (Greene, C R 9f, 40)

Properties — Colourless oil, insol Solidifies when cooled by solid CO. Easily reduced by sodium amalgam to benzene Aqueous HIAq at 250° reduces it to benzene Not affected by solid KOH at 250°, nor by alcoholic KOH or NH, (Kekı.lé)

Reactions -1 H2SO at 100° forms a mixture of 10do-benzene sulphonic acid, di 10dobenzene, and benzene sulphonic acid, in proportions varying with proportions of materials employed, strength of the said, temperature, and duration of the experiment (Neumann, A. 241, 47) -2 Silver nitrate does not act below 135°, but between 140° and 150° reaction takes place forming tri-nitro phenol, AgI, and metallic silver (Geuther, A 245, 99) —8 By heating with aluminium chloride there is formed ben'ene, di-10do benzenes, HCl, and 10dine (Dumreicher, B 15, 1868)

Dichlorade C.H.ICl. Formed by passing chlorine into liquid iodobenzene Formed also by passing chlorine into a solution of iodobenzene (5 g) in chloroform (15 g) (Willgerodt, J pr [2] 33, 154) Begins to decompose at 80°, and at 120° it is all broken up into Cl, and C,H,I may be kept in glass bottles, but if placed over H₂SO₄ it gives off chlorine It is decomposed by solution in alcohol, but it may be crystallised from chloroform as yellow needles It dissolves in benzene, glacial acetic acid, light petroleum, CS2 and ether As a reagent it displaces iodine by chlorine, turning KI, PbI₂, &c, into KCl PbCl₂, &c, with separation of iodine May therefore be used as a test for rodides It also converts alcoholic iodides (e.g. McI) into chlor ides. It is hardly attacked by cold aqueous NH, or NaOH

o Di 10do benzene C.H.I. [1 2] [27°] (287°) Preparation — Iodo aniline (10g) is dissolved in hot water (70 g) containing H₂SO, (9 g), KNO2 (45g) dissolved in a little water is added, and then an excess of solution of KI in aqueous HI (SG 11) After standing a few hours the oil that has separated is washed with KOHAq and distilled with steam (Korner a Wender, G 17, 486, cf Körner, G 4, 305) Long prisms or hexagonal tables Volatile with steam Sl sol water, sol alcohol

m D1 iodo benzene $C_aH_4I_2$ [1 3] [40°] (K), [37°] (R) (285°) From m 10do aniline by displacing NH, by I (Körner) Also from di 10do aniline by elimination of NH, (Rudolph)

Trimetric tables (from ether-alcohol)

p-Di-iodo - benzene C.H.I. [14] (Kekulé), [129°] (Körner) A product of the action of rodine chloride on NaOBz (Schutzenberger) and of 10dine and 10dic acid on benzene (Kekulé) Formed also from p 10do-aniline by the diazo- reaction (Kekulé, Z 1866, 688). Nacreous laminse Readily sullimed

Tri-iodo-bensene C.H.I.[124] Mol w 456. [76°]. A product of the action of iodine and iodic acid on benzene ("ekulé). Small needles May be sublimed

IODO-BENZENE-AZOXY- COMPOUNDS &

ABOXY- COMPOUNDS.

IODO-BENZENE O-SULPHONIC ACID C,H,LSO,H[1:2] From o-amido-bensene sulphonic soid by the disso-reaction (Bahlmann, 4. 186, 825) - KA'aq: crystals, sl. sol. water-BaA's. needles, sl sol. cold, v sol hot, water Ohloride C.H.I 50,01 [51°] Thick prisms (from ether)

Amide C.H.I.SO,NH, [170°]. White la-

minæ, sl sol water

Iodo-benzene p sulphonic acid C.H.I SO.H [14] From 10do benzene and fuming H₂SO₄ (Körner a Paterno, G 2, 448) Formed also from amido benzene p sulphonic acid by displacing NH, by I through the diazo- reaction (Lenz, B 10, 1135) Deliquezcent needles —NH, A'. minute needles —KA' needles —CaA'. —BaA'. minute needles—AA meedles minute plates, sl sol water—PbA'₂. a minute plates, sl sol water—PbA'₂. a minute plates, sl sol water—PbA'₂.

Chloride C.H.I SO Cl [87°] Lamine Amide C.H.I SO NH, [183°]. Crystalline Amide C.H. ISO2NH, [183°]. Crystalling powder, sl sol water, v so alcohol o IODO-BENZOIC ACID C.H. I CO2H [157°]

Formation -1 From o amido benzoic acid by the diazo reaction (Griess, C J 24,702) -2 By oxidising o iodo toluene with dilute HNO, (Kekulé, B 7, 1007) —3 From m iodo nitro benzene and alcoholic KCy at 200° (Richter, B

Properties -Long needles, may be readily sublimed SI sol hot water, v e sol ether and alcohol Gives salicylic acid when fused with potash

Salts - CaA', 2aq -BaA', 6aq ms Iodo benzoic acid CaHaI CO.H

[187°] Formation -1 From m amide benzoic acid by the diazo reaction (Griess, A 113, 334, 117, 1, Cunze a Hubner, A 135, 108, Grothe, J pr [2] 18, 324) —2 By heating benzoic acid (1 pt) with KIO, (2 pts) and dilute H₂SO₄ (Peltzer, A 136, 201) —3 By oxidising o iodo

toluene with chromic acid mixture (Korner, Z [2] 5, 637) -4 By heating dry silver benzoate with iodine at 150°-180° (Birnbaum a Reinherz, B 15, 456)

Properties - Needles, sl sol water, v sol alcohol May be sublimed Gives p oxy benzoic acid on oxidation Ammonia forms amido ben zoic acid

Salts — NaA'aq — MgA', 4aq — CaA', 2aq scales — CaA 3 nodules — BaA', 4aq needles sol alcohol.—MgA', 4aq needles.

Ethyl ether LtA'

Netrele C.H.I CN [41°] From m-amido

benzonitrile by the diazo reaction Needles p Iodo-benzoic acid C.H.I CO.H [20] (Beran, B 18, 137, Klingel, B 18, 2693) Formed by oxidation with chromic acid mixture from p ic lo-toluene (Körner, Z [2] 5, 327), from p 10do-phenyl acetic acid (Jackson a Mabery, Am 2, 253), or from p 10do acetophenone (Klin-Naureous scales (from alcohol) Nearly insol boiling water Converted by potash fusion into p oxy benzoic acid

Salts (Glassner, B 8, 562) — NaA' jaq colourless needles, v sol water — KA' — BaA', 1 jaq. long trimetric plates — CaA', aq — SrA', aq nacreous lamins. — ZnA', 4aq cubes

Methylether MeA' [114'] Long needles

(Schmidt a Schults, A, 207, 888)

Ethyl ether Eth' Oil

o IODO-BENZOIC ALDEHYDE C.H.I CHO [87°] Formed from o-nitro cinnamic acid by successive conversion into amido-, diazo-, and iodo cinnamic acid, and oxidation of the latter with KMnO, (Stuart, C. J. 58, 140).

p-Iodo-benzoic aldehyde C.H.I CHO. [73°]. Needles (Jackson a. White, B 11, 1042, P Am A

15, 269

p-IOD 3-BENZYL ALCOHOL C.H.,I CH.OH [72°] Prepared by heating p- odo benzyl bromide with NaOAc and aqueous NH, at 160° Formed also by heating p iodo benzyl bromide with water for a long time (Jackson, P Am A 13, 202, Jackson a Mabery, Am 2, 251, B 11, 56) Silky scales (from alcohol or CS,) or long needles (from water) Sl sol cold water, v sol alcohol, ether, benzene, and CS.

o IODO-BENZYLAMINE C H,IN te [2 1] C₆H₄I CH₂ NH₂ From o todo benzyl brom ide and alcoholic NH₂ (Mabery a Robinson, Am 4, 103) Liquid Absorbs CO, from the air -B',H,PtCl, minute yellow prisms

p Iodo benzylamine [4 1] C₄H₄I CH₂ NH₂ Formed by heating p 10do benzyl bromide with alcoholic NH, at 120° (Jackson a Mabery, Am 2, 257) Oil Absorbs CO from the air forming [240°], sol water and alcohol, sl. sol. ether — B'₂H₂PtCl₆ a carbonate[113°] —B'HCl slender white needles

D1-p-10do-d1 benzyl amine (C,H,I CH,),NH Formed, together with trip iodo tri benzylamine, by boiling p iodo benzyl bromide with alcoholic NH₂ (Jackson a Mabery, Am 2, 256, B 11, 58, P Am A 13, 209) White needles, insol water, v sol hot alcohol, ether, benzene, and C5

Salts - B'HCl thick white plates, sol. CS and HOAc, sl sol alcohol and benzene -B'HBr thick pearly prisms, insol water, sl soi aicohol sol ether, benzene, and CS₂ -B'₂H₂PtCl₂ minute yellow needles, almost insol water and alcohol

-B'_zH_zCO_z [113°] Crystalline

Tri-p iodo-tri-benzyl-amine (C,H,I CH2),N Formed as above (J a. M) needles (from ether), v sl sol hot alcohol, v sol ether, benzene, and CS. -B'2H2PtCl4 yellow needles, nearly insol water and alcohol

o IODO BENZYL BROMIDE C.H.I CH.Br Prepared by dropping bromine into o iodo toluene heated to 190°-200° (Mabery a Robinson, Am 4, 102, P Am A 17, 103) Thick flattened prisms (from ligroin), v sol ether, hot alcohol, benzene, CS, and chloroform, insol water Its vapour is very pungent Gives o iodo benzoic acid on oxidation with dilute

p Iodo bensyl bromide CaHaI CHaBr [79°] Prepared by heating p iodo toluene in bromine vapour at 115°-150° (Jackson, Am 1,93) Straw coloured needles, somewhat pungent Insol water and cold alcohol, sol hot alcohol, v sol ether Hardly attacked by CrO,

IODO-BENZYL CYANIDE v Netrele of Iopo-PHENYL-ACETIC ACID

o 10D0 BENZYLIDENE-MALONIC ACID C, H, IO, te C, H, I CH C(CO, H), [204°] Formed by heating equal weights of malonic acid and 10do benzoic aldehyde for several hours at 100° with half their weight of HOAc (Stuart, C J 53, 142) Decomposed on melting into GO, and q-iodo cinnamic acid

a-IODO-BENZYL-MALONIC ETHER

C.H. CH. CI(CO,Et), From sodium benzyl malonic ether and iodine (Bischoff a. Hausdo. fer, A. 239, 110). Oil. Decomposes on hydrolysis into benzoic aldehyde, alcohol, acetic acid, and

p-IODO BENZYL SULPHOCYANIDE C.H.I SCy [40°] Formed by boiling [40°] Formed by boiling p 10dobenzyl bromide with an alcoholic solution of potassium sulphocyanide (Jackson, P Am A 13, 207, B 11, 58) Long white plates (from alcohol) M sol hot alcohol, v sol ether, benzene, CS₂, and HOAc
IODO BETORCIN

C.HIMe(OH)2. [93°] Formed by the action of PbO and I (2 pts) on an ethereal solution (50 pts) of betorein (1 pt) Crystallised from light petroleum (Stenhouse a Groves, C J 37, 404) V sol ether, CS_2 , and

benzene

IODO BROMO- v BROMO IODO-

IODO BUTANE v BUTYL IODIDES

Di iodo butane C.H. i e CH, CHI CH2 CH2I (116° in vacuo) S G 2 291 From the corresponding di oxy butane and HI (Wurtz, Bl [2] 41, 362)

p IODO-ISOBUTYL BENZENE $C_gH_4(C_4H_9)I$ (256° cor) Formed by the action of HI on the diaro compound from p amido phenyl butane (Pahl, B 17, 1232) Colourless oil By HNO, it is oxidised to p iodo benzoic acid

IODO BUTYLENE C.H.I Crotyl vodide (132°) From tri oxy butane (butenyl glycerin), iodine, and phosphorus (Lieben a Zeisel, M 1, 836) Pungent liquid Combines with mercury forming an unstable crystalline compound

IODO-ISOBUTYL TOLUENE

 $\mathbf{C_6H_3}(\mathbf{CH_4})(\mathbf{C_4H_9})\mathbf{I}$ [1 3 6] [c 35°] Formed by diazotising amido tolyl isobutane and treating the product with HI (Effront, B 17,2325) Long white needles V sol alcohol On oxidation with HNO, at 200° it gives nitro tolyl isobutyric acid

a IODO n BUTYRIC ACID C,H,IO, CH, CH, CHI CO₂H [110°] (Fittig, B 9, 1194) From a crotonic acid and furning HI at 100° (Hemilian, A 174, 324, v infra) Monoclinic crystals (Haushofer, Z K 6, 135)

Ethyl ether EtA' (191°) Formed by boiling a bromo butyric ether with alcoholic KI

(Hell, B 6, 29)

β Iodo-butyric acid CH, CHI CH, CO,H Formed, in small quantity, in the preparation of

the preceding Liquid

According to Michael and Freer (J pr [2] 40. 95) HI unites with solid crotonic acid forming, contrary to the statement of Hemilian, only B 10do-butyric acid, of low melting point same acid is formed from liquid crotonic acid and HI Boiling water converts it into \$ oxybutyric acid Hot NaOHAq gives solid crotonic

γ-Iodo-butyric acid CH,I CH, CH,.CO,H [4]°] [41°] From the lactone of γ oxy butyric acid and HI (Henry, C R 102, 368, A Saytzeff, B14, 2826) Colourless plates, which become yellow in sunlight Sl sol warm water (difference from B isomeride), v. sol. methyl alcohol, ether, and

Methylether MeA' (199°) SG = 1666

Oil, with pleasant odour

Oil, with pleasant outer Iodo-isobutyric acid (CH₂)₂OI CO₂H (?) [36°] From me_hacrylic acid and furning HI at Ao / Futtic a Paul. A. 188. 58, 200, 67) Tables (from CS₂) or large prisms (from conc. HIAq) Sl. sol. water.

Di iodo isobutyrio acid C.H.I.O. [197°]. Formed by treating tri oxy isobutyric acid with HI and P and extracting the product with etner (E Fischer a Tafel, B 22, 108) Long needles, v e sol alcohol and ether

IJDO ISOBUTYRIC ALDEHYDE CH₂I)(CH₂)CH CO H or (CH₂)₂CI CO H

10 2 29

Preparation -By treating isobutyric alde hyde (22 5 c c) dissolved in 40 c c of alcohol, with iodine (25 g) and iodic acid (10 g) It is very difficult to obtain pure, 130 g of the crude body yielding not more than 1 g sufficiently pure for analysis Reduced silver removes the excess of rodine with the least loss of substance (Chautard, A Ch [6] 16, 160)

Properties —Her vy liquid, colourless when pure Its vapour 18, like its homologues, exceedingly irritating It is completely decom posed at 100°, and cannot be distilled even in Forms a crystalline compound with vacuo NaHSO, Is rapidly resinified by solutions of alkalis or mineral acids Combines with aniline, with elimination of water, giving a di amine Ag(C2H3O2) at 100° yields isobutyl acetate (114°) AgCN and AgSCN yield the corresponding cyano and sulphocyano derivatives

IODO CAMPHOR v CAMPHOR

IODO CAPROIC ACID v IODO HEXOIC ACID IODO-CAPRYL-BENZENE v Iodo octyl-

IODO CARBOSTYRIL v IODO OXY-QUINOLINE IODO CHELIDONIC ACID v CHELIDONIC

IODO CHRYSIN v CHRYSIN

o IODO CINNAMIC ACID C,H,IO, C₆H₄I CH CH CO₂H [214°] (G a H), [207°] (S) Formed by boiling o diazo cinnamic acid with aqueous HI (Gabriel a Herzberg, B 16 2037) Formed also by heating o iodo benzyl idene malonic acid to its melting point (Stuart, C J 53, 142) Crystals (from dilute alcohol)

m-Iodo - cinnamic acid CoH4I C2H2 CO2H [182°] Formed by boiling m diazo cinnamic acid with HI (G a H) Sol benzene, petro leum ether, and hot alcohol, sl soi water

p Iodo cinnamio acid C.H.I C.H. CO.H. [c 255°] Formed by boiling p diazo cinnamic acid with HI (Gabriel a Herzberg, B 16, 2040) Crystalline mass

IODO CODEINE v CODEINE

IODO - COMPOUNDS Organic compounds containing iodine attached to carbon

Formation -1 Unlike chlorine an 'bromine, iodine is not capable of directly displacing hy drogen, inasmuch as the HI produced would cause a reverse reaction But if iodic acid, mer curic oxide, or some other substance capable of removing HI be present, the substitution may take place (Kekulé, A 131, 281) In the case of aniline, the free HI combines with excess of ani line and thus iodo aniline may be formed Mercuric oxide will not induce the iodation of fatty compounds, but is especially useful in the case of phenols and oxy acids (Weselsky, A 174, 99). The operation is performed in boiling alcoholic solution, and an intermediate body appears to be mercuric iodate (Lippmann, B 7,1773) Aromatic hydrocarbons may be nodeted by heating with rodine and dry FeCl, (L. Meyer, A. 281, 195) — 2 By the action of HI on hydroxylic compounds. The alkyl rodides may be prepared in this way | does not act on acetyl p toluidine (B 11, 107) — by the action of HL or, better, of rodine and 8 By heating chloro-compounds with furning phosphorus, on the corresponding alcohols at HIAq (Lieben, Z 1868, 712) —9 Nitrogen rodide, The polyhydric alcohols give rise, in this way, to secondary alkyl rodides, the roding dis placing hydrogen attached to a penultimate atom of carbon thus glycerin gives isopropyl todide Iodides of acid radicles are formed by the action of iodide of phosphorus on the dry alkaline salts (Canours, A 104, 111) -3 By the union of HI with un aturated compounds This combination takes place more readily than in the case of HCl and HBr The rodine attaches itself to that one of the involved atoms of carron that is combined with the smaller amount of hy drogen, e g CH, CH CH2 + HI = CH, CHI CH3 4 From aromatic amido compounds by the diazo reaction This may be performed by heating the diazo compounds with HIAq, or with aqueous KI, $g = C_aH_s N_2 SO_4H + KI = C_6H I + N_2 + KHSO_4$ Also by Sandmever's reaction which consists in boiling the diazo compound with cuprous iodide, v Diazo coulot NDS -5 By gradually adding HNO, to a hot solution of the amine in HIAq (Losanitsch, B 18, 39) —6 By displacing Cl or Br by I by treatn ent with a metallic iodide The elements K, Mb, Ca, Sr Ba Al, Mn, and Co prefer chlorine and bromine to iodine and hence the iodides of these met ils when heated with chloro or bromo compounds produce iodo com pounds (köhnlein, 4 225, 194) Hhus propyl chloride is converted into propyl iodide by Cal, SrI₂, MnI₂, and CoI₂, while it is but slightly affected by Nil. and I el, is not affected by Snl, and is wholly decomposed by PI, The conver sion of benzyl chloride into benzyl iodide is par tially effected by BaI, at 15°, by ZnI₂ at 10°, by CdI₂ at 100°, and by PbI₂ at 160°. On the other hand isobutyl chloride is not converted into iodide at 70° by Bal, by ZnI or by CdI, while The substitution of CdI₂ at 135° decomposes it Cl in chloro acetic acid by I is partly effected by CdL, or TlI at 100°, and may be effected by Ba,I or ZnI, at 100° (Brix 1 225, 166) Potassium nodide is a very convenient reagent for the purpose (Perkin a Duppa, A 112, 125) but cannot be always depended upon, for though it displaces Cl by I in the case of epichlorhydrin, chloro lactic acid, dichlorhydrin, and mono and di chloro acetone, it does not act on di chlorinated ether, and it decomposes chloral into chloroform and CO2 Calcium iodide Cal, 3 aq is also an excellent reagent for converting chloro and bromo compounds into the corresponding iododerivatives (Spindler, A 231 257) Thus it con verts CH_Cl CH_Br into ethylene iodide, and CH_CHCBr into CH_CHI_2, but it fails with CH_2Cl CHCl_1 with CHCl_2CHCl_2 with CCl_1 CHCl_2. with C2Cl, with chloro benzene, and with chloral Dry Cal, requires a higher temperature (120°) before it reacts, and this decomposes many of the iodo compounds that should be formed— 7 Iodine chloride also acts as an iodating substance, especially upon aromatic amines it converts amiline (dissolved in HOAc) into di-iodo amiline (when 2 mols ICl are used) and tri-iodo-aniline (when 3 mols ICl are used) converts acetanilide into acetyl p-iodo aniline, m nitro aniline into di iodo m nitro-amiline, pnitro aniline chiefly into iodo-p-nitro-aniline, and p-toluidine into di-iodo-p-toluidine: but it

acting on dilute alcoholic solutions of the potassium derivatives of phenols, forms iodo phenols and ammonia (Willgerodt, J pr [2] 37, 446)

. Reactions -1 The displacement of iodine by chlorine or bromine may be effected by heating with the chloride or bromide of Hg, Cu, Ag, Sn, Pb, As, or Sb (v Chloro compounds and Bromo compounds) -2 Chlorine and bromine displace iodine directly -3 Sodium frequently removes iodine with case, $e \ g \ 2C_2H_3I + Na_2 = C_4H_{10} + 2NaI$ In like manner (by what is known as Fittig's re action) $C_6H_5I + C_2H_5I + Na_2 = C_6H_5C_2H_5 + 2NaI$

4 Water readily decomposes tertiary alkyl iodides, forming HI and a tertiary alcohol Methyl and ethyl alcohol at 100° act in like manner, forming a tertiary alcohol and MeI or I tI - 5 Silver obtained by reduction sometimes removes sodine eq 2CH, I CH, CO, H + Ag. = 2AgI + CO₂H CH₂ CH₂ CH CH₂ CO₂H

Some aromatic iodo compounds can take up chlorine, eq PhI gives PhICl, (Willgerodt, J pr
[2] 33, 154), C,H,Bri gives C,H,BriCl, while
C,H,Br,I gives C,H,Br,ICl, and C,H,(NO₂)I gives
C,H,(NO₁)ICl, C,H,(NO₂). I has no action

IODO m CRESOL C.H.MeI(OH) [1 x 3] Formed by adding rodine to a solution of mcresol in ammonia and alcohol (Willgerodt a

Kornblum, J pr [2:39, 289)

Iodo p cresol C₆H, Mc I OH [1 3 4] Formed by the action of dry iodine on sodium-georesol suspended in CS (Schall a Dralle, B 17, 2533) Inquid Volatile with steam

Methyl ether C.H.MeI(OMe) (238°), oil Di 10do o cresol C.H. MeI.(OH) [1342] Di 10do o cresol [70] Formed by the action of iodide of nitrogen upon the sodium compound of o-cresol (Will gerodt J pr 2] 37, 148 39, 289)

Acetyl derivative C.H.MeL(OAc) [56°] Tables

Picrate. [204°] Yellow crystalline aggregates

Di 10do m cresol C.H.MeI.(OH) I ormed to ether with 10do m cresol (W & K) Long needles, sol usual menstrua.

Di 10do p cresol C. H. MeI, OH [1 3 5 4] [61°] Formed together with the preceding (Schall a. Dialle, B 17, 2534) White tables soluble in alcohol, sparingly in water and ligroin. Volatile with steam

Acetyl derivative C.H Mel. (OAc) . [620] white tables

Benzoyl derivative C_cH₂MeL₂(OBz)

[130], glistening white prisms
Ethylether C.H.MeL.(OLt) [77°] White solid sol organic solvents (Willgerodt a Korn blum, J pr [2] 39, 289)

IODO CRESOL BULPHONIC ACID

 $[155^{\circ}]$ Formed C.H MeI(OH)SO,H [3 1 2 5] together with an isomeride, by the action of iodine on the potassium salt of o cresol sulphonic acid (kehrmann, J pr [2] 37, 338) plates (containing Saq) Converte Colourless Converted by attric acid into dinitro cresol [86°] Chromic acid forms iodo toluquinone [115°]

Salts - A'K hne needlos -A'Ba 4aq Di-iodo m cresol sulphonic acid $C_{e}HMeI_{r}(OH)(SO_{s}H)[3\ 6\ 2\ 1\ 4]$ [70°] potassium m cresol sulphonate by treatment with iodine (Kehrmann, J pr [2] 39, 892) Small

iodine (Louiziniani, γ γ [2] 57, 592) Similar meedles Oxidised by CrO₃ to di-todo-toluquinone 1000-ψ CUMENE O₄H₂IMe₃[1 2 4 5] Iodo-tri-methyl-benzene [37°] (258°) Formed by decomposing ψ cumene diazopiperidide with HIAq (S G 173) (Wallach a Heusler, A 243. 233) Formed also from ψ cumidine by dia o tising and herting the product, dissolved in H₂SO₄ with KI (Kurzel, B 22, 1586) Scales Treatment with H SO, forms two isomeric di 10do y cumene sulphonic acids y cumene sul phonic acid and iodo y cumene sulphonic acid One of the di 10do \(\psi\) cumenes melts at 74°, the other is an oil

10DO \(\psi\) CUMENE SULPHONIC ACID

C.HIMe.SO.H Formed as above Scales, m sol water

Salts —NaA'aq plates —BaA' aq ncedles IODO CYANETHINE v CYANLTHINE

IODO ETHANE v ETHYL IODIDE

D1-10do-ethane v ETHYLEVE IODIDE and ETHYLIDENE IODIDE

Tri-iodo-ethane C₂H₃I, ie CH, CI, [95°] Formed by the action of aluminium iodide upon CH₃ CCl₃ (De Boissieu, Bl [2] 19, 16) Yellow octahedra V e sol CS, benzene, and ether, v sol petroleum ether, m sol alcohol Smells faintly of iodoform

10D0-ETHYL ALCOHOL v GLYCOL todhydrin B-IODO ETHYL AMINE CH,I CH NH2

Hydriodide B'HI [194°] From vinylamine and cone HIAq (Gabriel, B 21, 1049)
Trime* crystals (from hot alcohol) V sol water When treated with KOH it gives a liquid, soluble in water, with a disagreeable odour

Picrate $B'C_0H_2(NO_1), \tilde{O}H_{\frac{1}{2}}$ aq [c 105°] (hydrated), [131°] (anhydrous) Short compact yellow prisms

Di-iodo ethyl-amine EtNI, v Ethyl di-iodo

amme, vol 11 p 474

wa DI IODO ETHYL BENZENE C,H,I, re C.H. CHI CH. I Styrene di wodide From styrene and a concentrated solution of iodine in KIAq (Berthelot, Bl 6, 295, 7, 277) Crystals, v sol Rapidly decomposes into iodine and metastyrene

10DO - ETHYLENE C2H3I 1 e CH, CHI (56°) SG 2 2 08 Vinyl rodide Formed by distilling ethylene iodide with conc alcoholic potash, the receiver being kept very cool, and the distillate finally mixed with water (Regnault, 15,69, E Kopp, C R 18,871) Also from ethylidene iodide (Gustavson, B 7,731) Formed also by the union of HI with acetylene (Beithelot, A 132, 122, Semenoff, Z 1865, 725) Oil, v sol alcohol and ether, with alliaceous odour

Di-iodo-ethylene C.H.I. 1e CHI CHI Acetylene di vodide [75°] (192° cor) SG 21 3 302 Formed by passing acetylene over iodine moistened with alcohol (Sabanejeff, A 178, 109, 216, 275, Plimpton, C J 41, 392) Elastic needles (from alcohol) It appears to be accompanied by a small quantity of a liquid isomeride S G 21 2 942 With alcoholic AgNO. it forms long needles of a compound C2H, I24AgNO3,

which is decomposed by HCl, giving off acetylene
Tetra - iodo ethylene Cl, Cl, Di carbo itetra-iodide [c 165°] Prisms Formed by the action of a solution of iodine in aqueous KI upon the cuprous compound of potassium propargylate. Formed also by the action of the

nodine solution upon setylene copper (Homolka a Stolz, B 18, 2283)

IODO-ETHYLIDENE DI-ETHYL DI SUL-PHONE CH₃ CI(SO₂Et)₂ [109°] From ethyl idene di ethyl di sulphone by boiling with iodine (Fromm, A 253, 146) Needles

IODO - DI - ETHYL OXIDE C.H.,IO 16 CH.I CH. OEt (175°) SG 2 1692 VD 691 (obs and calc) Formed by heating ethylene iodide with alcohol at 75° (Baumstark, B 7, 1172) Formed also from the mono ethyl den vative of glycol by treatment with iodide of phos phorus (Demole, B 9, 746) Pungent oil, not decomposed by water Alcoholic potash attacks it energetically, yielding CH_CH OEt (35°), and CH₂(OEt) CH₂(OEt) (1)² Be ling with re duced silver does not affect it

IODO-(B)-ETHYL-THIOPHENE

 $\mathbf{C}_{\mathbf{i}}\mathbf{H}_{\mathbf{2}}(\mathbf{C}_{\mathbf{2}}\mathbf{H})\mathbf{IS}$ Oil Formed by the action of iodine upon (8) ethyl thiophene in presence of HgO (Bonz, B 18, 551)

IODO-FLUORO-BENZENE v FLUORO 10DO BENZENE

IODOFORM CHI, w 394 [119°] S G 2 Tri rodo methane Mol

Depression of freezing point of benzene by rodoform Raoult, A Ch [6] 2, 88, Paterno, B 22, 465

Formation -1 By heating alcohol with iodine and caustic or carbonated alkalı (Serullas A Ch [2] 2c, 314) Indoform is formed in like manner by the action of iodine and potash or aldehyde, acetone, lactic acid, and many other substances (cf vol 1 p 96) —2 From chloro form and HI (Baeyer, B 5, 1094) 3 By heat ing chloroform with Cal, at 75° (Spindler, A 231, 263) -4 Together with carbamic ether, by the action of iodine on sodium carbamic ether

(Mulder, R T C 7, 333)

Preparation -1 Alcohol containing about 20 pc aldehyde is mixed with ten times its weight of aqueous NaOH, todine is added, and the mixture stirred from time to time iodoform quickly separates in the cold (Gunther, Ar Ph [3] 25, 373) -2 To prepare iodoform R Rother (Ph [3] 4, 593) heats 32 pts iodine, 32 potassium carbonate, 16 alcohol of 9) per cent and 80 water, till the mixture becomes colour less, then decants the clear liquid, collects the separated crystals of iodoform, and mixes the filtered liquid with 16 to 24 pts hydrochloric acid and 2 to 3 pts potassium dichromate liquid is then neutralised with potassium car bonate, and 32 pts more of that salt are added, together with 6 pts iodine and 16 alcohol reaction having been completed at the heat of the water bath, the product is treated as above, whereby a fresh quantity of iodoform is ob tained -3 By the action of excess of sodium hypochlorite on an aqueous solution of acctone (6 pts), potassium iodide (50 pts), and NaOH (2 pts) (Suillot a Raynaud, Bl [3] 1, 3)

Properties -Hexagonal yellow tables, a c= 1 9015 (Rammelsberg a Kokscharoff, C C 1857, 524, of Dogiel, N Petersb Acad Bull 20, 337) Above its melting-point it partly decomposes, giving off iodine and HI Has a peculiar per sistent odour Volatile with steam Insol water, acids, and alkalis, v so' alcohol, ether, and fixed and volatile oils An alcoholic solution of iodoform is decomposed under the influence of light. The decomposition is accelerated by dry oxalic acid, iodine and methylene iodide are produced (Mulder, R T C 7, 310, cf Humbert, J Ph [3] 29, 352) Does not in the least hinder the putrefaction of pancreas at 35° (Boillat, 7 pr 188, 308)

Detection -An alcoholic solution of iodoform warmed with aqueous KOH and a little phenol forms a red substance, which dissolves in dilute alcohol, giving it a crimson colour (Lust-

garten, M 3, 717).

Reactions —1 Heated in a sealed tube at 150°, either alone or with iodine, it yields methylene iodide and brown products (Hofmain, C J 13, 65) -2 Bromine gives bromoform (Löscher, B 21, 410), ut an excess of Br at high temperatures forms Cb., -3 Distilled with HgCl, it yields CTTCl, I (Schlagdenhauffen, J Ph [3] 29 247) -4 Mercuric oxide forms CO, formic acid, figl., and water -5 Boiling aqueous KOH forms a little potassium formate -6 Boiling alcoholic potash forms methylene iodide (Brun ing, A 104, 187, Butlerow, C R 47, 595) -7 NaOEt forms methylene iodide, NaI, aldehyde, acrylic acid, and CH, CH(OEt) CO,H (Butlerow, A 107, 110, 114, 204, 118, 325)—8 K,SO, forms CH₂(SO,K)₂ (Strecker, A 148, 90)—9 By the copper zinc couple iodoform may be reduced to methane (Gladstone a Tribe, C J 28, 508) 10 Unites with PEt, forming C₁₉H₄₆P₂I₂ (Hof mann, Pr 10, 189)—11 PCl, forms chloroform 12 When made into a paste with moist finelydivided silver, acetylene is at once given off mixture of ppd silver and copper is even more effective (Cazeneuve, C R 97, 1371) -13 Silver nitrate acts readily at ordinary temperatures, forming AgI, nitric acid, and CO, so that by nitrating the liberated acid an estimation of the quantity of iodoform present may be formed (Greshoff, R T C 7, 342)—14 Iodoform exposed to direct sunlight is completely oxidised by air, forming CO, iodine, and water (Daccomo, G 16, 247) -15 Mercuric acetate is reduced by iodoform to mercurous acetate, CO, being evolved It does not reduce mercuric nitrate (although chloral forms, in this case, mercurous chloride) (Cotton, J Ph [5] 16, 481) -16 Isobutyl alcohol (200 g) mixed with sodium (20 g) and iodoform (100 g) gives a violent reaction, the products being formic acid, isobutyric acid, pentenoic acid, CMe₂ CH CO₂H [70°], isobutyl oxy isobutyric soid C₄H₂O CMe₂ CO₂H, a lactone of an oxy octoic acid, isobutylene, methyl isobutyl oxide, methylene li isobutyloxide, a compound C12H26O30 and other bodies (Gorboff a Kessler, J R 1887,

10D0-FUMARIC ACID C2HI(CO2H)2 Iodomalero acid [184°] Formed by dissolving acetylene di carboxylic acid in strong aqueous HI (Baudrowski, B 15, 2697) Fine glistening Very soluble in water, alcohol, and orystals

Salts -A''HK small sparingly soluble stals $-A''Ag_2$ crystalline pp -A''Pb 2aq crystals -A"Ag,

crystalline pp ACID C₁₁H₂₁IO₂ 16
From hen-CH₂I CH₂ (CH₂), CO₂H decenoic soid and HI (Ph Brunner, B 19, 2224) Crystalline

10DO HEPTOIC ALDEHYDE C.H., I CHO. B.G 10 281 Vol. III. Formed by treating heptoic water excepting the silver salt.

(conanthic) aldehyde (75 g) diluted with alcohol (100 c c) with iodine (50 g) and iodic acid (20 g). The crude product is purified by treatment with reduced silver The yield is very bad (Chautard, A Ch [6] 16, 170) Very unstable liquid with arritating odour Decomposed by heat Easily decomposed by KOH, NaOH, ammonia, and mineral acids

Reactions -1 Nitric acid gives heptoic aldehyde and heptoic acid -2 Silver acciate forms octyl acetate (208°) -3 By heating iodo heptoic aldehyde (120 g) dissolved in alcohol with silver cyanide (67 g) there is formed C₆H₁₂Cy CHO (177°) S G ¹² 913 This is a colourless liquid which reduces Fehling's solution and ammoniacal AgNO, but does not form crystalline compounds with aniline or phenyl hydrazine -4 Silver sulphocyanide forms the corresponding sulphocyano heptoic aldehyde -5 Heating with

aniline forms C.H., I(NHC, H.).

IODO HEPTYLENE C.H., I v.e

Pr.CH., CI CHMe or Pr.CH. CI CH, Me 150°) From heptinene (q v) and HI (Morris, C J 41, 179)

1000 HEXANE v HEXYL TODIDE

Di 10do hexane C,H12I, 16 CH, CHI CH, CH, CHI ČH, Hexylene sodsde S G 2 2 024 Formed by heating di allyl in a sealed tube for 5 hours with excess of conc HIAq at 100° (Wurtz, A Ch [4] 3, 129), or better, by passing gaseous HI into strongly cooled diallyl (Sorokin, J pr [2] 23, 18) Oil, gives off iodine when heated With sodium it gives hexplane and hexenyl 10d1de Alcoholic potash forms diallyl Silver acetate forms hexylene acetate C. H 12(OAc)2, whence baryta forms di oxy hexane

Tetra 10do hexane C.H.10I. [above 107°] From diallyl and iodine (Berthelot a. De Luca,

4 100, 363)

TETRA IODO-HEXINENE v Tetra rodide of DIPROPARGYI

IODO-HEXOIC ACID C.H., IO, Formed by mixing hydrosorbic scid with cone HIAq at 0° (Fittig, A 200, 44) Oil, turning yellow on exposure to light May be reduced by sodium amalgam to n hexoic acid

IODO HEXYLENE C.H.,I t.s

CH, CH CH, CH, CHI CH, Hexenyl wodrde Diallyl hydroiodide (165°) SG 2 1497 Formed, together with di iodo hexane, by the action of HI on diallyl (Wurtz, A Ch [4] 8, 155) Formed also by the action of alcoholic potash or of an alloy of tin and sodium on di iodo hexane CH, CHI CH, CH, CHI CH, When treated for 24 hours with moist Ag₂O it forms diallyl, hexylene, and two liquids C₆H₁₂O (c 135°) and C12H22O (180°)

Iodo hexylene C_cH₁₁I (131°) SG 10 1 92 Formed from the hexenyl alcohol obtained by distilling glycerin with lime (Destrem, A Ch. [5]

27, 58)

Iodo hexylene C.H., I (142°-145°) pinacone hydrate and HI at 160° (Bouchardat, Z 1871, 699) Reduced by tin and HCl to hexylene.
Bromine gives crystalline C.H., Br.
10D0 HIPPUBIC ACID C.H., INO, 1.6

NHBE CHI CO2H (?) Formed by treating a boiling alcoholic solution of hippuric acid with nodine (Maier, Z 1865, 415) White needles De-composes at 90°. All its salts are soluble in Iede-hippuric acid C₆H₄I CO NH CH₂ CO₂H Formed by the action of aqueous HI on the sulphate of diazo hippuric acid (Griess, Z [2] 4, 725, B 1, 190) Laminæ, v sol cold alcohol and ether, m sol hot water, nearly insol cold water The iodine is not easily removed

IODO-HYDROCINNAMIC ACID v Ioro-

PHENYL PROPIO IC ACID

DI-10D0-HYDROQUINONE C₄H,I₂(OH)₂ [5 8 4 1] [145°] Formed by boiling di-iodo-quinone [180°] with a dilute solution of SnCl₂ (Seifert, J pr [2] 28, 438, Kehrmann, J pr [2] 37, 837) Long colourless needles (from hot water) Volatile with steam

Di-iodo hydroquinone C_eH₂I₂(OH), [142°] From di-iodo quinone [159°] and aqueous SO, (Metzeler, B 21, 2555) White needles, v sol hot water, alcohol, ether, and HOAc, m sol benzene Reoxidised by FeCl₂ to di iodo

quinone

Ds-acetyl derivative C_sH₂I₂(OAc), [148°] Needles or plates (from alcohol), insol water, v sol alcohol and ether, si sol cold HOAc

IODO HYDROTHY MOQUINONE

C_sHMePrI(OH)₂ [5 2 6 4 1] [74°] Obtained by reducing iodo thymoquinone with SnCl₂ (Kehrmann, *J pr* [2] 39, 392) Colourless prisms, v sol organic solvents

IODO HYDRO TOLUQUINONE

C.H.MeI(OH)₂ [6 2 4 1] [111°] From the corresponding quinone, by reduction with SnCl₂ (Kehrmann, J pr [2] 39, 392) Soft silky aggregates of needles, sol organic solvents

IODOL v Tetra iodo pyrrole IODO-LACTIC ACID v Iodo oxy propionic

IODO-MALEÏC ACID v Iodo fumaric acid

IODO MELLIOTIC ACID Methyl derwature $C_{be}H_{11}IO_{2}$ to $C_{e}H_{4}(OMe)$ $C_{2}H_{3}I$ $CO_{2}H$ From the methyl derivatives of (a) and of (b) coumaric acid and fuming aqueous HI in the cold (Perkin, C J 39, 429) Aqueous Na₂CO₂ forms $C_{e}H_{4}(OMe)$ CH CH₂ and CO_{2}

IODO METHANE v METHYL IODIDE
Di-iodo-methane v METHYLENE IODIDE

Tri-iodo methane v Iodoform

Tetra-iodo-methane CI. Carbon tetra iodide S G 22 4 32 Formed by mixing CCl. with alu minium iodide dissolved in CS. (Gustavson, A 172, 173, C R 78, 882) Formed also by heating CCl. with CaI. 3½ aq at 75° (Spindler, A 231, 264) Dark red regular octahedra (Friedel, BI [2] 21, 482) Sol CS., alcohol, ether, and MeI May be kept for some days, but gradually decomposes The decomposition is hastened by both CS. and CO. Above 80° it quickly splits up into carbon and iodine Converted into iodo form by boiling with aqueous HI, and even by boiling with water Scarcely attacked by aqueous potash or H.SO. Chlorine converts it into CCl. Br gives CBr.

IODO-DI METHYL AMINE v Di methyl-

sodo-amine under DI METHYL AMINE

INDO DI-METHYL-ANILINE C₂H₁₀IN te C₂H₁ NMc₂. [79°] Formed by adding rodine to a solution of di-methyl aniline in CS₂ (Weber, B 10, 765) Formed also by the action of cyan ogen rodide on di-methyl aniline in the cold, hieat being evolved and HCy given off (Merz a-Weith, B 10, 757). White lamine, sol alcohol

and HOlAq Not ettacked by caustic sods When heated above 80° it rives off HI and leaves a residue which forms a deep violet solution in alcohol—B' F.PtCl_k

ICDO-TRI METHYL-BENZENE v. Iodo V

IODO METHYL-BUTYL-BENZENE v IODO-BUTYL-TOLUENE

DI IODO METHYLE DI ETHYL DI-SULPHONE CI.(SO.Et). [177°] Formed from methylene di ethyl di sulphone I, and KIAq, by exposure to sunlight (Fromm, A 253, 161) Needles, si sol boiling water

DI-IODO DI-METHY. OXIDE C₂H,I₂O te (CH,I)₂O (219°) From dry 'oxymethylene' (formic paraldehydr' and gaseous HI (Tish-

tschenko, J R 1887, 464) Oil

IODO TRI METHYL PIPERIDINE C₂H₁₆IN [60°] Formed by heating ethylidene discettaine with HI (E Fischer, B 17, 1796) Colourless rectangular prisms Nearly insol water —B'HI very sparingly soluble

Iodo-tetra-methyl-piperidine C₈H₁₈NI [90°]. Formed by heating triacetonine with HI at 150° (E Fischer, B 17, 1791) Easily soluble in alcohol and ether, insol water Colourless tables (from ether)

IODO DI METHYL THIOPHENE C₆H,IS ι θ
CI CMe
S (97°) From di methyl thiophene

CH CMe (from coal tar), iodine, and HgO (Messinger, B 18, 1638) Oil

Iodo - tri - methyl - thiophene C,H,IS ie CMe CMe | S Formed by the action of iodine

CMe CI (48 g) and HgO (21 g) on tri methyl thiophene (12 g) dissolved in ligroin (24 g) (Zelinsky, B 21, 1837) Non volatile oil

(a) IÓDO NAPHTHALENE C₁₀H,I (305°)
Formation —1 By adding rodine to a solution of mercury dinaphthyl Hg(C₁₀H₁), +2I₂
= HgI₂+2C₁₀H I (Otto, A 147, 173) —2 From diazo naphthalene sulphate and LI (Nolting, B 19, 135)

Properties Thick yellowish oil, not solidified at -17° Miscible with alcohol, ether, CS, and benzene Alcoholic potash at 160° forms some naphthalene Boiling HIAq (127°) completely converts it into naphthalene When a solution in C5, is boiled with aluminium chloride there is formed naphthalene, iodine, and tarry matter, but no (β) iodo naphthalene (Roux, Bl [2] 45, 517)

Picric acid compound [127°]. Golden

yellow needles

(β) Iodo-naphthalene C₁₀H,I [55°] Pre pared by the action of HI on (β) diazo naphthalene sulphate (P Jacobson, B 14, 804) Colourless plates, sol ether, alcohol, and HOAc Volatile with steam

(a, a,) Di-iodo-naphthalene C₁₀H₄I₂ [1 4] [110°] From (a) iodo (a) nitro naphthalene by reduction, and treatment of the resulting iodo naphthylamine with H₂SO₄ and NaNO₂, followed by HI (Meldola, C J 47, 522) Needles (from alcohol)

 $(a_1\beta_2)$ -Di-iodo-naphthalene $C_{10}H_aI_1$ [1 2]. [81°]. From (β) -iodo- (α) -nitro-naphthalene in

the same way as the preceding (Meldola) Scales (from alcohol)

(β) - 10D0 - NAPLTHALENE SULPHONIC ACIDS C₁₂H₄I SO₂H Two isomerides are formed by sulphonating (β) iodo-naphthalene (Arm strong a Wynne, C J Proc 3, 22) One of the isomerides forms the salts KA' aq and BaA'₂4½aq, both crystallising in hexagonal scales, the other forms the salts KA' aq crystallising in lamine, and BaA'₂2aq in flat n edles

(1, 5) Iodo naphthal me sulphonic acid C_{1.}H₄I(SO₂H) [' 5] [129°] Formed from (a) diazo naphthalene sulphonic acid and warm HIAq (40) c) (Mauzelius, B 22, 2820) Colourless tables (containing Jaq) v so. water

Salts—A'K aq plates m sol water—A'Naaq ınııstınct n.edles—AAg plates S 66—A'₂Ca 2aq scales, sl sol water—A'₂Ba aq scales S 23 (ın the cold) S 1 at '00°—A'₂Mg needles sl sol water—A'Zn 6aq scales, m sol water—A'₂Cu 4aq glenish white needles, sl sol water—A'₂Pb 4aq sl sol. water—A'Mn 4aq ındıstınct crystals sl sol water

Methyl ether MeA' [60°] Prisms v sol Lt₂O, al sol cold EtOH

Ethyl ether EtA' [74°] Six sided tables

▼ sol It,O

n Propyl ether PrA' [67°] Colourless
tables

Isopropyl ether PrA' [90°] Prisms Chloride CieHellSO,Cl [114°] Monoclinic prisms v sol hot AcOH, sl sol ligroin

Bromide [153°] Prisms

A mide C₁₀H₄I(SO₂NH₁) [239°] Scales (a) IODO (β) NAPHTHOL C₁₀H₄I(OH) [12] [945°] (M), [c 100°] (W) Prepared by dissolving equal parts (20 g) of (β) naphthol, lead acetate, and dried sodium acetate in HOAc, cooling, and gradually adding iodine (35 2 g) dissolved in hot HOAc. The product is ppd by water and recrystallised from dilute alcohol (Meldola, C J 47, 527) Formed also by the action of iodide of nitrogen on a dilute alcoholic solution of sodium (β) naphthol (Willgerodt, J pr [2] 37, '48)

Properties — Long colourless needles, sl sol boiling water, v sol organic solvents Volatile with steam Sol cold dilute KOHAq, decomposed by hot alkalis Nitric acid liberates iodine

KMnO, gives phthalic acid
(a) IODO (a) NAPHTHYLAMINE

C₁₀H₄(NH₂) [4 1] From (a) node (a) nitro naphthalene, zinc dust, and HOAc (Meldola, C J 47, 521) Its solution rapidly oxidises in the air forming a red colouring matter —B'₂H₂SO₄ tolerably stable white needles

Acetyl derivative C₁₀H₄I(NHAc) [196°] From the preceding by boiling with Ac₄O (M) Needles (from alcohol) Gives a nitro derivative

[286°]

10D0-0 NITRO ANILINE C₆H₁I(NO₂)(NH₂) [521] Formed by heating di nodo nitro-benzene [168°] with alcoholic NH₃ at 170° for several days (Körner, G 4, 386) Large steel blue laminæ (from alcohol in ealed tubes) yellow by transmitted light Does not melt at 220° Not attacked by nitrous ether

Iodo o-nitro-aniline C₄H₄I(NO₂)(NH₄) [4 2 1] [122°] Formed by warming a solution of the acetyl derivative of p iodo-aniline in HOAc with

HNO, (Michael a Norton, B 11, 109) Long orange-yellow needles (from alcohol)

Iodo-p-nitro-aniline C_eH₂I(NO₂)(NH₂) [2 4 1] [105 5°] Prepared by the action of iodine chlor ide (2 pts) on p nitro aniline (1 pt) dissolved in dilute HClAq (Michael a Norton, m 1, 26°2, B 11, 113) Long yellow needles —B'HCl [163°]

Di 10do-m-nitro-aniline C_eH₂I(NO_e)₂(NH_e) [4 2 3 1] (145 5°] Formed by passing iodine chloride (3 pts) into a solution of m nitro-aniline (1 pt) in HClAq (Michael a Norton, Am 1, 255, B 11, 112) Long slender yellow needles, v sol cold alcohol, sl sol acetic ether, insolwater Its hydrochloride is not decomposed by water

D1-todo-p-nitro-aniline C_eH₂I₁(NO₂)(NH₁) [6 2 4 1] [244°] Prepared by the action of iodine chloride (2 mols) on p intro aniline dissolved in chloroform (M a N) Yellow prisms with blue fluorescence (from alcohol) Sl sol hot alcohol, sol CHCl₂ and EtOAc, v sol hot nitro benzene It is not basic

o IODO NITRO BENZENE C. H.I(NO.) [12] [49°] Formed, together with the p isomeride, by treating iodo benzene with HNO. (Korner, G 4, 305) The p isomeride crystallises first from alcohol Long flat lemon yellow needles Gives a little o iodo amiline and much amiline on reduction

m Iodo-nitro benzene C_6H , $I(NO_2)$ [1 3] [36°] (c 280°) I ormed from m intro aniline by dis placing NH₂ by I through the diazo reaction (Griess, Z 1866, 218) Monoclinic plates, a b c = 2 296 1 1 129 (Panebianco G 9, 360) The same body is perhaps formed by the action of ICl on sodium m nitro benzoate (Schutzenberger a Segenwald, Rép Chim pure, 1802, 144)

a Segenwald, Rep Chim pure, 1862, 144)
p Iodo-nitro-benzene C₆H₄I(NO) [14] [171°]
The chief product of the action of fuming HNO₂
upon iodo benzene (hekulé, A 137, 129) Obtained also from p nitro aniline by the diazo
reaction Pale yellow needles

Di chloride C.H.(NO)ICl. Formed by passing Cl into a solution of iodo nitro benzene in chloroform (C Willgerodt, J pr [2] 33, 160) Hardly sol CS, Et.O, or light petroleum Sol. CHCl. and benzene At 150° it gives off Cl., leaving C.H.(NO₂)I With alcohol it reacts forming aldehyde, HCl and C.H.(NO₂)I.

Iodo-di-nitro-bensene C₄H₁I(NO₁)₂ [1 2 4] [899] Obtained by intrating o or p-iodo nitrobenzene with H SO₄ and HNO₄ (Körner, J 1875, 322) Yellow tricininc crystals, a b c = 1 63 t 1 940 (La Valle, G 10, 3) V sl sol cold alcohol. Hot dilute KOH forms di nitro phenol Alcoholic NH₁ gives di nitro aniline, though the de composition is incomplete in the cold

Iodo di-nitro-bensene C₄H₃I(NO₂)₂ [1 2 6] [114°] Formed in small quantity, together with the preceding, by treating o iodo nitro benzene with HNO₃ mixed with H₂SO₄ (Körner, G 4, 305) Orange triclinic tables (from alcohol) More sol alcohol and ether than the preceding Converted by heating with alcoholic NH₃ into di nitro-aniline [138] May be reduced to phenylene m-déamine.

Iodo-tri nitro-bensene C₄H₄I(NO₂), [1 2 4 6]. [164°] From chloro tri nitro-benzene and alcoholio KI (Hepp, A 215, 361) Golden needles

Converted by boiling aqueous KOH into picric

Di-iodo nitro-benzene C_eH₂I₂(NO₂) [1 3 4] [168°] Obtained from m di 10do belizene by dissolving in hot fuming HNO, (Körner). Trimetr γ octahedra, abc=6471 458 (La Valle, G 10, 2) Sl sol ether, v sl sol cold alcohol By heating for a few days with alcoholic NH, at 170° it forms iodo nitro aniline

Di-iodo-nitro-benzene C₆H₃I₂(NO₂) [1 2 4?] [112 5°] Formed by dissolving o di-iodo benzene in fuming HNO, and, after a few minutes, diluting with water (Körner a Wender, G 17, 491) Lemon yellow needles or small prisms

(from alcohol)

(a)-IODO-NITRO-BENZOIC ACID C,H,INO, $C_6H_3I(NO_2)(CO_2H)$ [3 2or6 1] Formed, together with the two following, by heating m 10do-benzoic acid with conc HNO3 (Grothe, pr [2] 18, 324, Cunze a Hubner, A 135, 106) Sl sol water, especially if HCl be present -Gives o amido benzoic acid on reduction NH, A'aq -NaA' 3aq -CaA' 2aq -SrA', 4aq -BaA'2 3aq Ethyl ether EtA' [84°]

(β)-Iodo nitro-benzoicacid C_eH₃I(NO₂)(CO₂H) [8 6or2 1] [174°] Formed as above water, especially if HCl be present Melts under May be reduced to o amido benzoic acid -NH, A'aq -LıA'aq -NaA' 4aq -KA'3aq -CaA' -SrA', -BaA', 6aq

[64°] Ethyl ether EtA' Yellow plates

(γ)-Iodo-nitro-benzoic acid

 $C_{\bullet}H_{\bullet}I(x, \mathcal{O}_{\bullet})(CO_{\bullet}H)$ [3 x 1] [192°] Formed as above \forall sol water, but does not melt under it —NaA'aq sılky yellow needles —CaA'₂ 3\2q -SrA'₂ 4aq —BaA'₂ 3aq

Iodo-nitro-benzoic acid C_sH_sI(NO₂)(CO₂H) [210°] Formed by heating p 10do [4 3 1] benzoic acid with fuming HNO, (Glassner, B 8, 562) Nearly insol water, v sol alcohol -NaA'aq —KA'aq —CaA', 1 aq

(a,a,)-10D0-NITRO-NAPHTHALENE O,H,1(NO₂) [4 1] [123°] Formed from acetyl-(a)-naphthylamine by nitration, saponification, diazotisation, and treatment with HI (Meldola, C J 47, 519) Minute white needles (from hot alcohol) Sol benzene, HOAc, and acetone May be reduced to (a) naphthylamine

 $(a_1\beta_2)$ -Iodo nitro-naphthalene C10HeI(NO) [12]. [1085°] Formed from the mother lauor of the preceding (Meldola) Yellow scales May

be reduced to (B)-napthylamine

 $(\beta_2 a_1)$ -Iodo-nitro-naphthalene C10HeI(NO2) [2 1] T [88 5] From acetyl (a) nitro (β) naphthylamine by saponifying with hot dilute H.SO., and subsequent displacement of NH₂ by I (Mel dola, C J 47, 520)

 (a_i) -IODO (β_2) NITRO- (a_1) NAPHTHOL $C_{10}H_3I(NO_2)(OH)[4\ 2\ 1]$ [146°] Form Formed by boiling acetyl (4, 2, 1)-iodo nitro-naphthylamine with strong caustic alkali (Meldola, C J 47, 524) Yellow needles (from alcohol) Insol cold water, si. sol hot water and hot benzene, v sol alcohol, scetic acid, and acetone Yields phthalic acid on oxidation Its K and Na derivatives form minute orange needles, m sol cold water — {C_{1.6}H_{.5}I(NO₂)},Ba 3aq bright red amorphous {C₁₀H₂I(NO₂)}₂Ba Saq bright red amorphous pcwder, almost insol. boiling water, deflagrates on ignition

(α_i) - IODO - (β_i) - NITRO - (α_i) - NAPHTHYL-AMIN - Acetyl derivative

 $C_eH_sI(NO_s)(NHAc)[4\ 2\ 1]$, [236°] From acetyl-10do naphthylamine by warming its solution in HOAc with HNO, at 75° (Meldola, C J 47, Straw coloured needles (from alcohol). Sublimes while melting More difficult to saponify by H₂SO₄ than the bromo-compound IODO NITRO-0 CXY BENZOIC ACID

 $O_7H_4INO_5$ 1 e $C_8H_2I(NC)(OH)(CO_2H)$ From (5, 2, 1) nitro oxy benzele acid by treatment in alcoholic solution with I and HgO (Weselsky, A 174, 108) Slender yellow needles -KA' 2aq -C,H2K2NO, 3aq —BaA', 6aq

Iodo nitro o oxy ben hic acid

 $C_6H_2I(NO_2)(OH)(CO_2H)$ [204°] From (5, 2, 1). iodo oxy benzoic acid by nitrai on (Hubner, B 12, 1347)

Iodo nitro m oxy benzoic acad

C_eH₂I(NO₂)(OH)(CO₂H) Formed by treating an alcoholic solution of nitro m oxy benzoic acid with I and HgO (Weselsky, A 174, 103).

Lemon-yellow crystals, sl sol water, v sol cold alcohol—BaA', 6aq minute red needles

Iodo nitro p oxy benzoic acid

C_sH₂I(NO₂)(OĤ)(CO₂H) From nitro p oxybenzoic acid, iodine, and HgO (W) Lemonyellow needles -- BaA'24aq flat red needles

BaC.H.INO. 2aq short dark red needles DI-IODO DI NITRO DI-OXY-DI-PHENYL SULPHONE C12HeI2N2SOs 2 6

 $SO_2(C_6H_1I(NU_2)OH)_2$ [205°] Formed by heat ing iodine (50 g) dissolved in alcohol with a mixture of di nitro-di oxy di phenyl sulphone (34 g) and HgO (21 6 g) at 100° (Annaheim, B 9, 660) Needles (from HOAc), insol water and alcohol Decomposes alkaline carbonates -

Na₂C₁₂H₄L_{N2}SO₂2aq IODO O NITRO PHENOL C.H.INO, too. C₂H₄I(NO₂)(OH) [110°] (Armstrong, Watts' Dict Ed 1 Suppl 2, 917, B 6, 649) Formed by the action of iodine and HgO on c nitro phenol dissolved in HOAc (Busch, B 7, 462, cf Armstrong) Short yellow needles, v sol hot water, alcohol, and ether Moderately volatile with steam — KA'aq garnet red plates with green lustre (A), v e sol hot water and alcohol

Iodo-p nitro phenol C₆H₃I(NO₂)(OH)[2 4 1]. [93°] (Körner, Armstrong) Formed by the action of iodine and HgO on p nitro phenol dissolved in HOAc (Korner, Bull Acad Belg [2] 24, 166, Busch, B 7, 462) Also from nitro amido phenol by the diazo reaction (K) Yellow needles —NaA'2½aq (K) —KA' ½aq (B) Nitrie acid converts it into iodo di nitro phenol [106°].

Iodo di-nitro phenol

C₆H₂I(NO₂)₂(OH)[6 4 2 1] [106°] (A), [108°] (W) Formed from (4, 2, 1) di nitro phenol by [106°] (A), [108°] treatment with iodine, potassium iodate, and potash (Körner, G 4, 397) or with iodine and HgO (Armstrong, B 6, 649, Weselsky, A 174, 111) Formed also from di nitio amido phenol by the diazo- reaction (A), and by the nitration of the preceding 10do nitro phenol (A) Long slender lemon yellow needles (from hot water) SI sol het water —KA deep orange needles, v sol hot, sl sol cold, water —CaA' 25aq: orange red plates, v sol. hot water

Iodo-di-nitro-phenol C_eH₂I(NO₂)₂(OH)[4 6 2 1] [113°] Formed from (6, 2, 1)-di-nitro phenol by treatment with sodine

and rodic acid (Körner, G 4, 897) or with iodine and HgO (Armstrong, B 6, 649) Long, lerron-yellow needles (from water), v sl sol water and alcohol The potassium derivative forms magnificent crimson needle. with green and golden lustre, sl sol water The silver and golden lustre, al sol water derivative forms small brownish red needles

Di 10do-o-nitro-phenol C.H.I.(NO.)(OH)[6421] [98°] From o nitrophenol, iodine, and iodic acid in alkaline solu tion (Körner) Slender dark yellow needles (from ether alcohol), sl sol water, v sol boil ing alcohol and ether —NaA'aq dark brown prisms, with golden lustre —KA' very soluble

reddish brown needles

Di iodo p nitro phenol C.H.I.(NO.)(OH\[6 2 4 1] [157] (K) From p nitro phenol, iodine, KIO, and potash (K., cf Seifert, J pr [2] 28, 437) Also from p nitro phenol o sulphonic acid iodine in alcoholic colution and Iodine in alcoholic solution, and HgO (Post a Brackebusch, A 205, 91) Formed also by treating nitro-o oxy benz oic acid with iodine and HgO (Weselsky, A 174, 177) Large colourless prisms (from ether) turning yellow on exposure to air Decomposes a little above its melting point -KA' golden needles with violet iridescence -NaA' 2aq efflorescent orange laminæ

Di 10do nitro phenols appear also to have

been obtained by Piria (A 198, 268)

TODO NITRO PHENOL BULPHONIC ACID C.H.INSO, 1 e C.H.I(NO2)(OH)(SO3H)[2 6 1 4] Formed when todine and HgO are added to an alcoholic solution of o nitro phenol p sulphonic acid (Armstrong a Brown, C J 25, 869) —KA' yellow scales, composed of short needles, sl sol water - K₂C₆H₂INSO₆ red crystals -BaA'₂4aq pale yellow silky needles, sl sol water

Iodo nitro phenol sulphonic acid $C_sH_2I(NO_2)(OH)(SO_3H)[6\ 4\ 1\ 2]$ Formed, to gether with di iodo p nitro phenol, by treating an alcoholic solution of p nitro phenol o sul phonic acid with iodine and mercuric oxide (Post a Brackebusch, A 205, 88) — Salts CaC, H₂INSO, 3aq coarse yellow needles, m sol water—BaC, H₂INSO, 3aq long yellow needles, m sol water—Pb₂(OH)₂C, H₂INSO, 2½aq yellow crystalline pp DI IODO NITRO-RESORCIN

C.HI. (NO2)(OH)2. From nitro resorcin in alco holic solution by alternate addition of iodine and mercuric oxide (Weselsky, A 174, 111) Golden n edles

10D0 NITRO-THIOPHENE C,H,I(NO,)S [74°] Formed by nitration of iodo thiophene (Kreis, B 17, 2073) Glistening yellow prisms IODO NITEO-TOLUENE C,H,INO,

O₆H₂MeI(NO₂)[1 4 2] [61°] (286°) From (4,2,1) di-nitro toluene (Heynemann, A 158, 337)

Pale yellowish crystals V e sol CS, and ether Iode - nitro - toluene C, H, MeI(NO,) [1 4 3] [56°] From p toluidine by nitration and displacement of NH, by I (Beilstein a. Kuhlberg, A 158, 844) Large flat needles, v sol. boiling alcohol

Iodo - nitro - toluene $C_{x}H_{x}MeI(NO_{x})[1\ 2\ x]$ [104°]. Formed by nitrating o-iodo-toluene (B Minute needles

Iodo nitro-toluene (?) [109°] Formed by nitrating m-iodo-toluene (B. a. K.). Small meedles.

Iodo di-nitro-toluene C.H.MeI(NO.),[1 4 5 3] [138°] Formed by nitrating p-iodo toluene (Glassner, B 8, 561) Crystals IODO-OCTINOIC ACID C. H., IO. i.e

C,H,)2CI CO,H Iodo-di-allyl acetic acid Arom (C.H.) C(OH) CO₂H (17 g) and cold fuming HIAq (45 g) (Schatzky, J R 17 78) Crystals, insol. water, v sol alcohol and ether Easily decomposed

p 1000 n-0CTYL-BENZENE $C_{14}H_{21}I$ s.e $C_{5}H_{4}(C_{5}H_{1})I$ [1 4] (319°) Heavy oil. Formed by diazotising p amido phenyl octane, and treating the diazo-octyl benzene with HI (Beran, B 18, 136) On oxidation with CrO, it gives ptodo benzoic acid Iodo octyl benzene obtained by the action of iodine and HgO upon n-octylbenzene is described by Ahrens (B 19, 2720) as an oil, solidifying at -4°, and completely decomposed by distillation

p-Iodo sec-octyl-benzene C_cH₁(C_cH₁₇)I [1 4] p Iodo capryl-benzene (305° uncor) Formed by diazotising p amido phenyl sec octane and treating the diazo capryl benzene with HI Heavy oil. V sol ether and acetic acid, sl sol alcohol It is oxidised by CrO, to p iodo benzoic

acid (Beran, B 18, 142)

IODO (a) OCTYL THIOPHENE C, H, IS se $C_4H_2SI(C_8H_{17})$ [c 0°] SG $\frac{29}{20}$ 1 2614 From octyl thiophene (10 g) in ligroin by treatment with iodine (10 g) and HgO (11 g) (Schweinitz, B 19, 644) V sol ether, cannot be distilled IODO OLEIC ACID v IODO-STF-RIDENIC

IODO ORCIN C,H,IO, s.e C,H,MeI(OH)... Formed by dissolving orcin (1pt) and iodine (2 pts) in ether (6 pts), and gradually adding finely powdered litharge (9 pts) The ether is distilled off, and the residue recrystallised from benzene (Stenhouse, Pr 22, 53) Prisms, decomposing when heated alone or with water Sl sol cold water, v sol hot water, alcohol, and ether Has not the astringent sweet taste of orcin

Tri iodo-orcin C,H,I,O, se C,MeI,(OH). Formed by adding to a dilute aqueous solution of orcin a quantity of ICl,, not quite sufficient to ppt all the ordin, and crystallising the pp first from CS_2 and then from boiling alcohol (Stenhouse, C J 17, 327) Large transparent plates, tinged with brown V sol CS_2 , V e sol ether, m sol alcohol, msol water Becomes brown at 100° Dissolves with decomposition ın aqueous KOH Decomposed by hot H.SO. and by hot HNO.

Iodo-(B)-orcin v Iodo betorcin

DI-IODO-ORSELLIC ACID Methyl ether C.H.I.O. te C.H.I.O.Me Methyl dr-rodo-dr-oxytoluate Formed by adding a dilute solution of chloride of iodine, containing excess of iodine, to a cold saturated aqueous solution of methyl orsellate (Stenhouse, A 149, 295) Needles from CS2), sol benzene, CS2, alcohol, and boiling water Decomposed on fusion

Ethyl ether C.H.I.O.Et Formed 12 like manner Small needles, almost insol.cold water, m. sol benzene, CS, and boiling alcohol Decom-

posed on fusion

10DO-0 OXY-BENZOIC ACID C,H,1O, 1.4. C₄H₂I(OH)(CO₂H)[3 2 1] Iodo-salicylic acid. [198°] Formed, together with the following compound, by boiling a solution of salicylic acid

and iodine in alcohol, and separated by frac tionally crystallising the product from water (A Miller, C J 41, 406, A 220, 124) Long needles, v sol water Gives a violet colouration with FeCl, Gives the corresponding di ony benzoic acid on potash fusion —BaA', 3 mq
concentrically grouped needles S 5 at 8°

Iodo-o-oxy benzoic acid C.H.I(OH)(CO,H)
[5 2 1] [196°] (G), [193 5°] (F), [197°] (M)
8 11 at 20°, 1 at 100° (L)

Formation -1 As above -2 Together with di- and tri-iodo oxy-benzoic acids, by fusing salicylic acid (1 mol) with iodine (1 mol), and treating the product with aqueous KOH (Kolbe a Lautemann, A 115, 157) -3 By dissolving equal weights of rodine and salicylic acid in 80 p c alcohol, boiling for 3 hours, evaporating, and dissolving in aqueous Na_2CO , (Lautemann, A120, 299) -4 From salicylic acid, iodine, and HgO (Hlasiwetz a Weselsky, B 5, 380, A 171, 99) -5 By agitating a hot solution of salicylic acid (1 pt) in water (25 pts) with a mixture of nodine (1 pt) and nodic acid (1 pt), keeping the liquid hot for some time The resulting acid is converted into sodium salt, and the satingneedles of the salt of the di iodo acid separated, if necessary by hand picking, from the lancet shaped laminæ of the mono iodo acid (Liechti, **A** Suppl 7, 129, H Fischer, A 180, 346) —6 From the corresponding nitro oxy benzoic acid by reduction to oxy amido benzoic acid and ex change of NH2 for I by the diazo reaction (Gold berg, J pr [2] 19, 368, P F Frankland, C J 37, 749) -7 By warming dry silver salicylate with iodine (Birnbaum a Reinherz, B 15, 458)

Properties -Long needles (from water), sl sol water, v sol alcohol and ether violet colour with FeCl, On potash fusion at 200° it gives di oxy benzoic acid [197°] When suddenly heated it splits up into CO2 and iodo

phenol

Salts -NaA'aq S 77at 20° (L) -KA'3aq Salts—NaAaq S 77at20' (L)—RA saq laminæ S 19 at 20° (L)—NH₄A' $3\frac{1}{2}$ aq needles S 95 at 20° (L)—BaA'₂4aq waity scales S (of BaA'₂) 8 at 8° (M), 13 at 20° (L)—BaC₂H₄IO₂ 2aq tufts of small needles (L)—CaA'₂6aq—MgA'₂baq—PbA'₂—AgA' yellowish

Ethylether EtA' [71°] (Schmitt, Z 1864,

821).

Iodo-m-oxy-benzoic acid C₆H₄I(OH)(CU₂H) by alternately adding iodine and HgO to oxy benzoic acid dissolved in 90 pc alcohol, and separated by solution in boiling water (Weselsky, A 174, 105) Slender needles, sl sol cold

Iodo-p-oxy-benzoic acid C_eH₃I(OH)(CO₂H) [841] [160°] (P) S 18 in the cold

Formation -1 By boiling a solution of poxy-benzoic acid for a few minutes with iodine and rodic acid (Peltzer, A 146, 288) -2 From p oxy benzoic acid dissolved in alcohol by alternate addition of iodine and HgO (Weselsky, A 174, 99)

Properties - Small needles (from water) Decomposes at 1.2° May be sublimed below its melting-point V e sol alcohol and ether

Gives with FeCl, a dingy brown pp Salts.—NaA' 6aq monoclinic efflorescent erystals.—Na₂C,H₂IO, 6aq. hygroscopic silky

needles (from alcohol) -BaA', 7aq tarles - AgA white pp

C_eH_sI(OMe)CO,H Methylderivative Iodo anisic acid [235°] S (cold ether) 7 Formed by leating anisic acid with iodine and iodic acid at 150° (P) Formed also by oxidation of the methyl ether of 10do p cresol (Schall a Dralle, B 17, 2533) The same, or an isomeric acid, is formed from amido anisic acid by the diazo reaction (Griess, Pr. 10, 309) Plates (S a D) or needles (G) Nearly insol boiling water, m sol alcohol —NaA'2aq concentrically grouped needles -BaA', 3aq vitreous prisms CaA', 3aq nacreous laminæ—PbA', (at 100°); ourdy pp —AgA' micro-crystalline laminæ

D1-iodo-o oxy-bel-zoicacidC,H I (OH)(CO,H) Di rodo salicylic acid S 07 at 15°, 15 at 100° (L) Formed, together with iodo o-oxy-benzoic acid, by the action of iodine and aqueous potash, of rodine and rodic acid, or of rodine and HgO upon salicylic acid (Lautemann, A 120, 304, Liechti, A Suppl 7, 141, Demole, B 7, 1439, Weselsky, A 174, 103) Formed also by heating dry silver salicylate with iodine (Birn baum a Reinherz, B 15, 459) White felted mass (from hot water) V sol alcohol and At 197° (L) or 220° (W) it begins to de compose, giving off iodine It gives a violet colouration with FeCl. On potash fusion it gives

tri oxy benz_ic (? gallic) acid and pyrogallol Salts -NaA'2 aq long flat needles, mostly grouped in druses S 2 at 20°, much less soluble in water than iodo o oxy benzoic acid —KA' aq minute thick prisms S 553 at 20° V sol alcohol, sl sol ether —NH,A' aq arbo rescent groups of small needles S 32 at 20°—BaA'₂3aq needles S 074 at 18° V sl sol alcohol—BaC,H.I,O, 1½aq small silky tablets, v sl sol water, forming an alkaline solution -CaA', 5aq needles S 086 at 18°

Di 10do-p oxy benzoic acid

C₆H₂I₂(OH)(CO₂H) Formed, together with 10do p oxy benzoic acid, by iodation of p oxy benzoic acid (Peltzer) Small needles (from dilute al cohol) Nearly insol boiling water, v e sol Decomposes when heated alcohol and ether without previous fusion Cannot be sublimed -NaA'7aq tufts of delicate, iridescent, efflores cent needles, v sol water - Na C,H,I,O, 6aq trimetric tables —BaA'₂ gelatinous pp got by adding alcohol to its aqueous solution — CaA', 2aq nacreous laminæ —PbA', bulky pp Swells up like mercuric sulphocyanide when heated $-AgA' - Ag_2C_7H_2I_2O_8$

Tri lodo o oxy benzoic acid $C_0HI_s(OH)(CO_2H)$ [c 157°] Obtained in small quantity in preparing mono , and di iodo o oxy benzoic acids by the action of iodine and KOH Weselsky (A on salicylic acid (Lautemann) 174, 104) could not obtain it by treating salicvile acid with iodine and HgO. Tufts of needles (from alcohol). Insol water, sol alcohol and ether Decomposed by alkalis into CO, and a red body C_eH₂I₂O (?) Its sodium salt is a

grey-green mass, v sl sol water

IODO p-OXY-BENZOIC ALDEHYDE C,H,IO, i.e C.H.I(OH) CHO [199°] Formed by heating the dilute alcoholic solution of p oxy benzoic aldehyde with iodine for some hours (Herzfeld, B 10, 2196) Sl sol, water and benzene, v sol

alcohol and ether Converted by potash fusion into protocatechuic said

Iodo di-oxy-benzoic aldehyde Methyl 1erivative C.H.IO, s.e C.H.I(OH)(OMe) CHO Iodo vanillin [174°] Formed by warming vanillin with an alcoholic solution of iodine (Carles, Bl [2] 17, 12) Needles Sl sol cold alcohol and ether

Di iodo-di-oxy-benz ic aldehyde Methyl derivative C.HI.(OL.)(OMe) CHO Formed like the preceding, using more iodine (C) Crys tals, insol chloroform, sol alcohol and ether

a IODG 8-OXY-PHENYL PROPIONIC ACID C.H.O. re C.H. CH(OH) CHI CO.H Formed by treating cinnamic acid with an aque ous solution of rodine ch'oride, the compound CaH, CHCl CHI CO2H being probably first formed (Erlenmeyer a Rosenhek, B 19, 2464) Large crystals (from benzene) With HCl it gives the compound C₁₈H₁₆ClIO₄, which may possibly be C.H. CH-CH.C(OII) CO C(OH) CHLCHCLC.H.

Exo Iodo-o oxy phenyl-propionic acid Methyl derivative C.H. (OMe) C.H. I CO.H Formed by the combination of the methyl derivative of (a) or (B) coumaric acid with HI (Perkin, C = J = 39, 429) Decomposed by aqueous Na.CO, into CO₂, HI, and C_bH₁(OMe) C₂H₃

TETRA IODO-DI OXY DI PHENYL **PHONE** C₁₂H₄I₄SO₄ i e SO₂(C₆H₂[†] OH)₂ [260°-270°] S G $\stackrel{11}{\sim}$ 2 797 From di oxy di phenyl From di oxy di phenyl sulphone by treatment in alcoholic solution with iodine and HgO (Annaheim, B 9, 1150) Minute needles (from HOAc) Decomposes on fusion Insol cold alcohol, nearly insol boiling alcohol and HOAc

β IODO-α OXY-PROPIONIC ACID C,H,IO, re CH,I CH(OH) CO,H Iodo lactic acid [101°] (M), [85°] (G) Formed by treating \$\beta\$ chloro a oxy propionic acid with KI at 10° ((rlinsky, B Prepared by the addition of HI to 6, 1257) sodium glycidate (Mclikoff, B 14, 937) prisms, v sol water, alcohol, and ether verted by alcoholic KOH into glycidic acid -AgA' white unstable pp — ZnA', crystalline powder (M) or tables (G)—CaA', 3aq amor crystalline phous (M)

DI IODO-OXY-PYRIDINE C,NH,L,(OH) [2 4 5] (?) [209°] Formed by heating an al kaline solution of pyridine di carboxylic acid (quinolinic acid) with iodine and KI at 180°-200° Small flat needles Sol hot acetic acid and am j l alcohol, v sl sol boiling water, alcohol, ether, or chloroform Dissolves in dilute alkalis -C,NH,I,(ONa) 3aq colourless glistening scales, al sol aqueous NaOH (Pfeiffer, B 20, 1352)

10D0-(Py 3)-OXY QUINOLINE C.H.NOI: c. CI CH CH CI or C.H. (OH) Iodo 'N C(OH)

carbostyril [276°] Formed by boiling o amido phenyl propiolic acid C,H,(NH2) C C CO,H with dilute HI (Baeyer a Bloem, B 15, 2149) Sublimable

ORSELLIC ACID

IODO-PENTANE v AMYL IODIDE Di-iodo-pentane C.H., I. . c (CH, CHI), CH (c 182°). Formed by heating methylene di-

methyl diketone (CH, CO), CH, with HI at about 90° (Combes, A Ch [6] 12, 235) Liquid, begins to decompose at its boiling point

IODO-PENTINENE C,H,I+ e (CH,),CH C CL (140°) Formed from the silver derivative of (CH₂)₂CH C CH by treatment with a solut on of iocine in KI (Eltekoff, J R 9, 225) Laquid Gives (CH₂)₂CH C CH when heat'd with NaOEt.

DI-IODO DIPHENIC ACID v DI-IODO-DI-PHENYL DI CARBOXYLIC ACID

o IODO-PHENOL C.H.,IO to [2 1]C.H.,I(OH) [4301

Formation -1 Probably occurs among the products of the iodation of phenol (Schutzen berger a Sengenwald, C R 54,197, Körner, A 137, 197, Hlasiwetz a Weselsky, Sitz W 60 [2] 290, Lobanoff, B 6, 1251) -2 By the action of iodine on sodium phenol suspended in CS_2 (Schall, B 16, 1897) -3 By heating the chloride or sulphate of o diazo phenol with KI, distilling the product with steam, and recrystal lising from water (Nölting a Wrzesinsky, B 8, 820, Nölting a Stricker, B 20, 3018, Bl [2] 49,659, Neumann, A 241, 68) -4 By adding powdered rodine to a dilute alcoholic solution of phenol, mixed with ammonia (Willgerodt, J pr [2] 37, 446)

Properties - White needles, v sol water and other ordinary menstrua According to Schall (B 20, 3363) it forms in crystalline branches, melting at 43° or needles melting at 40° Nitric acid attacks it, setting iodine free, but chlorine does not do so, but forms chloro nodo phenol Potash fusion at 165°-250° yields pyrocatechin Not affected by air and light Cold conc H2SO4 produces di iodo phenol (Neumann, B 20, 581)

m-Iodo phenol [3 1] C.H.I(OH) [40°] Prepared from m 10do aniline by diazo- reaction.

The product is distilled with steam, extracted with ether, and recrystallised from ligroin (N a S) It hay be prepared in like manner from mamido p enol, by diazotising and heating the product with Sus KI Needles (from ligroin)
May be sublin. V sol alcohol and ether It does not give off ind a when treated either with HNO, or with chlorine It yields resorcin when fused with KOH

p Iodo phenol [4 1] C₆H₄I(OH) [94°] Formation -1 In the iodation of phenol -2 From p amido phenol by diazotising and heat ing the product with KIAq (N a S) -3 A by product, together with di and tri iodo-phenol, in the formation of o iodo phenol from iodine, ammonia, and an alcoholic solution of phenol

Willgerodt, J pr [2] 37, 446)
Properties - Long needles Nitric acid sets When iodine free, but chlorine does not do so heated with conc H,SO, it gives (1, 3, 6) di iodophenol [72°] Potash fusion gives resorcin at high temperatures

D1-iodo-phenol $C_0H_2I_2(OH)$ [4 2 1] [72°] Formed by mixing o iodo phenol (10 g) with H.SO, (30 g) at -10° (Neumann, A 241, 71) Formed also in like manner from p-10do phenol White needles (from water) Volatue with DI-IODO-DI-OXY TOLUIC ACID v Dr 1000- steam Boiling HNO, converts it into picric

> Acetyl derivative C.H.I.(OAc) Long flat trimetric prisms (from dilute alcohol); a.b.c = 7311832.

Di-iodo-phenol C₆H₂I₂(OH) [68°] Formed as a by product in the action of iodine upon phenol-sodium suspended in CS₂ (Schall, B 16, Apparently formed also 1899, 1902, 20, 3364) in the action of iod_ne chloride on phenol (S a S) White glistening plates Volatile with steam -C.H.l. ONa needles

Acetyl derivative C.H.I. (OAc) [107° un-

cor], small prisms

Bensoyl derivative C₆H₂I₂(OBz) [96°

uncor]

Di iodo phenol C₆H₂I₂(OH) [150°] Formed by the action of iodine and HgO on an alcoholic solution of phenol (Hlasiwetz a Weselsky, Sitz W 60 [2] 290, C C 1870, 63) Silky felted needles (from dilute alcohol), v sol alcohol, ether, and CS₂. May be sublimed Not affected

by boiling alcoholic KOH

Tri iodo-phenol C_eH₂I₃(OH) [6 4 2 1] [155°] Formation -1 By treating phenol with a considerable quantity of ICI, and exhausting the product with boiling alcohol in which tri iodophenol is not very soluble (Schutzenberger, Bl [2] 4, 102) -2 From phenol, iodine, and KOH (Lautemann, A 120, 307) -3 From phenol, iodine, and iodic acid (Körner, A. 137, 213) 4. From salicylic acid, iodine and iodic acid (Kekulé, A 131, 231) -5 Formed as a by product from the action of iodine on phenol sodium suspended in CS₂ (Schall, B 16, 1899) —6 By the action of iodide of nitrogen on a dilute alco holic solution of sodium phenolate (Willgerodt,

J pr [2] 37, 447)
Properties - Needles (from dilute alcohol) Decomposed on fusion M sol alcohol verted by excess of ICl into per chloro-phenol HNO, gives picric acid HCl and KClO, give

chloranil

DI-IODO-PHENOL SULPHONIC ACID

C.H.L.(OH)(SO.H)[6 2 1 4] [120°] Formed by adding a solution of KI and KIO, to one of phenol p-sulphonic acid in aqueous HCl (Kehrmann, J pr [2] 37, 11, 334, 359, Osterr ayer, J pr [2] 87, 215) Monoclinic prisir e sol water, but ppd by HCl or H, SO,, decomposes at 190° Converted by nitric acid; 'o pieric acid Chro mic acid oxidises it to di iodo quinone

Salts-KA' 2aq long needles or thick prisms —NaA' 3aq sol water, commercially known as 'sozodole'—C₆H₂K₂I₂SO₄ dimetric prisms — BaA', 3aq shining needles, v sl sol water — ZnA', 6aq long needles The copper

HI on the diazo- compound derived from benz idine (Schmidt & Schultz, B 12, 489) leaflets

o-IODO PHENYL-ACETIC ACID C.H.,IO. te C.H.I CH, CO2H [96°] Prepared by digesting its nitrile with fuming HCl for four hours at 126° The nitrile is formed by treating o-iodobenzyl bromide with KCy (Mabery a Robinson, Am 4, 102) Slender needles (from water), so hot water, alcohol, ether, CS,, and ligroin - AgA curdy pp; sl sol water Slender needles (from water), sol

p-Iodo-phenyl-acetic acid C.H.I CH2.CO2H. [185°] Prepared by heating its nitrile with fuming HClAq in sealed tubes at 100° (Jackson, Mabery, Am. 2, 253, P Am A 18, 205, B 11, 56). Narrow white plates (from water) with

agreeable odour like sweet allysium, v sol hot water, alcohol, ether, benzene, and CS, Gives p-1 do benzone acid on oxidation—BaA', aq minute white needles, v sol water—AgA' glistening plates, sl sol boiling water

Nitrile C.H.I CH, CN p Iodo benzyl cyan-ide [50 5°] Prepared by boiling p-iodo benzyl bromide with alcoholic KCy Pearly plates insol water, v sol alcohol, ether, and CS

IODO PHENYL-ACE, YLENE C.H. C CI Obtained from phenyl acetylene (Holleman, B 20,

8080) Brownish-yellow liquid^c
IODO-PHENYL-ACRYLIC ACID v IODO CIN

Exo-IODO-DI-PHENYL-AMYLIDENE-DI-AMINE C₁, H₂₁N₂I s.s C₂H₂I(NHPh), Formed by heating iodo isovale c aldehyde with aniline (Chautard, A Ch [6] 16, 169) Large brownish yellow needles, v sol water and alcohol, m sol other solvents Decomposed on fusion uncrystallisable salts

DI - IODO - DIPHENYL - DI - CARBOXYLIC ACID C_{1.}H_sI₂O_s to C_cH_sI(CO₂H) C_cH_sI CO₂H [262°] Prepared by the action of HI on the diazo-derivative of di amido di phenyl dicar boxylic acid (Schultz, B 11, 217, A 196, 21, 203, 95) Amorphous, v sl sol boiling water,

v sol alcohol, acetone, and ether

DI IODO PHENYLENE OXIDE so called Tetra 10do diphenylene quinone C,H2I2O Formed in the action of iodine and KOH upon o, m, or p oxy benzoic acid and on phenol (Lautemann, A 120, 309, Kammerer a Benzinger, B 11, 557) Formed also by boiling tri todo phenol with aqueous Na CO₂(L), and by distilling di 10do diphenyl dicarboxylic acid with lime (Schultz, B 11, 217) Reddish brown powder, insol water, alcohol, ether, chloroform, and benzene Dissolves in CS, with deep red colour Boiling KOHAq has little action on it Conc HNOs forms pierie acid It decomposes at 200° Aqueous SO, at 100° forms colourless $C_{12}H_{6}I_{4}O_{2}$

DI-exo IODO-DI-PHENYL-ETHYLENE O14H10I2 te CIPh CIPh Formed by heating diphenyl acetylene (tolane) with dry iodine and crystallising from chloroform (E Fischer, A 211, 233) Rose coloured plates, ▼ sl sol alcohol

Decomposed by heat

ω IODO DI - PHENYL - ETHYLIDENE - DI AMINE C14H15IN22 e CH2I CH(NHPh) Obtained by heating 10do acetic aldehyde with excess of aniline (Chautard, A Ch [6] 16, 155) needles or tables Cannot be melted wi' lout de composition V sol alcohol, sol ether, benzene and CS2 With strong acids it forms uncrystallisable salts, v sol water and alcohol

DI-p-IODO DI-PHENYL-GUANIDINE C₁₃H₁₁Î₂N₃ is CN₂H₃(C₆H₄I)₂? From p-10do-aniline in ethereal solution and CyCl (Hofmann, A 67, 148) Crystalline -B', H, PtCl

Tri-p-iodo-tri-phenyl-guanidine C, H, I, N, From di p-iodo di phenyl thio-urea and iodine

(Losanitsch, B 5, 158)

Exo-IODO-DÍ-PHENYL-HEPTYLIDENE-DIAMINE C.H., I(NHC.H.). Formed by heating todo heptoto aldehyde with aniline (Chautard, A Ch [6] 16, 178) Lemon yellow deliquescent tables, v sol alcohol, al sol benzene and CHCl. Decomposes on heating Does not give crystalline salts

p-10D0-PHENYL-HYDBAZINE $C_tH_tN_2$ to $C_tH_tNH_tN_1$ [10°°] Formed, by reducing the diazo-derivative of p-10d0 aniline [60°] with an excess of SnCl₂ (Neufeld, A 248, 98) Silky needles (from hot water), v sol alcohol, other, chloroform, benzene, and dilute HOAc With acetone it forms CoH, I N2H CMe2 crystallising from petroleum ether in white plates [114° With acetic aldehyde it gives C.H.I N2H CHMe [107°] crystallising from petroleum ether in yellow needles

Di-iodo-phenyl-hydrazine C.H.I.(N H.)
[4 2 1] [112°] From di 10do aniline by diazo C,H,I2(N H,) tising and reducing with SnCl, (Neufeld, A 248, White silky needles, v sol alcohol, ether, and benzene, al sol hot water and petroleum ether The hydrochloriue [162°] crystallises

from water in white needles

Di-iodo-s di-phenyl hydrazine C₁₂H₁₀I₂N₂ i e [81] C.H.I NH NH C.H.I [13] Hydrazo discoo benzene [90°] Formed by heating the azoxy compound C. H. I N.O C. H. I with alcoholic ammonium suiprade at 100° (Gabriel, B 9, 1408) V sol ordinary solvents

Di-10do-s di phenyl hydrazine

[41] C₆H₄I NH NH C₆H₄I [14] Formed by heating the corresponding azoxy compound with alcoholic ammonium sulphide at 100° (G) Flat needles, decomposed before melting

p IODO PHENYL OXAMIC ACID

C.H.I NH CO CO.H [c 200°] S 072 at 25° Formed by the action of a coholic potash on the di iodo di anilide of oxalic acid (Dyer a Mixter, Am 8, 357) Long white fibres Sol alcohol and ether -- *BaA'₂ white pp -- *AgA' pp -- KA' sol hot water white

p-10D0 PHENYL PHTHALIMIDE

$$C_rH$$

(2)C=N C_sH_sI [227°-228°] Prepared by heating p iodo aniline with phthalic anhydride (Gabriel, B 11, 2261) Needles V sol C_eH_e, less sol ether

o 10DO PHENYL PROPIONIC ACID

C.H.IO, s.e C.H.I C.H. CO.H o Iodo hydrocin namic acid [103°] Plates (from water) Formed by reduction of o iodo cinnamic acid (Gabriel a Herzberg, B 16, 2037)

m Iodo-phenyl propionic acid C.H.I C H. CO.H m-Iodohydro cinnamic acid [66°] Colourless plates Formed by reduction of m 10do-cinnamic acid (Gabriel a. Herzberg, B

16, 2039)

p-Iodo-phenyl-propionic acid C.H.I.O.H. CO.H. p Iodo hydrocinnamic acid [141°] White prisms Formed by reduction of p-10do-cinnamic acid with HI and P (Gabriel a Herzberg, B 16, 2010)

8-Iodo-phenyl-propionic acid

C.H. CHI CH. CO.H [120°] Formed by adding fuming HIAq to a concentrated aqueous solution of β oxy phenyl propionic acid (Glaser, A 147, 97) Formed also from cinnamic acid and cone HIAq in the cold (Fittig a. Binder, A. 195, 183) Small crystals (from CS₂) Decomposed on fusion Boiling with water converts it into HI and connamic acid Aqueous Na, CO,

Formed by heating \$\beta\$-iodo propionic aldehyde with excess of aniline (Chautard, A Ch [6] 16, 159) Brownish yellow needles or tables, v sol. all ordinary solvents Decomposed by heat with-Gives no crystalline salts out previous fusion

DI-IODO-DI PHENYL SULPHIDE C, d.I.S e e (C.H.I).8 [139°] Formed by heating di phenyl sulphide with rodine and rodic acid in sealed tubes Got also from di amido di phenyl sulphide by the diazo reaction (Krafft, B 7, Laminæ

p'IODO PHENYL THIOCARBIMIDE

C.H.INCS [65°] Formed by the action of nodine on an alcoholic solution of di p nodo diphenyl thio urea (Losanitsch, B 5, Crystals

DI p 10D0-DI PHENYL-THIO UREA

C₁₁H₁₀L₂N S *.e CS(NH C_eH₄I)_p [173°] From
p 10d0 annline, alcohol, and CS₂ (Losanitsch, B From V sl sol alcohol and ether

10DO 150 PHTHALIC ACID C.H.I(CO.H). [6 3 1] [204°] Formed by oxidation of 10dotolyl methyl ketone C.H.MeI CO CH. [1 2 5] with CrO. (Klingel, B 18, 2701) Fine white needles. Sublimable V sol alcohol, acetic acid, and ether, insol cold water

Salts - A"Ba very sparingly soluble fine white needles - A'Ca microscopic needles - $A''Ag_i^*$ white crystalline pp $-\bar{A}''Cu^*$ green crystalline pp

IODO PROPANE v PROPIL IODIDE

Di iodo-propane C,H,I, i.e. CH, CHI CH,I Propylene iodide S G 12 249 From propyl-From propylene and iodine (Berthelot a De Luca, C R 39, 743) From allyl iodide and gaseous HI at -18° (Malbot, C R 107, 114, Bl [2] 50, 449) Liquid Split up by alcoholic potash into iodine and propylene

Di-iodo-propane CH,I CH, CH,I Tra methylene todide (227°), (169° at 170 mm) SG \$\frac{1}{2}\$ 2 5631, \$\frac{1}{4}\$ 2 5962, \$\frac{25}{85}\$ 2 5614 Obtained by heating s di oxy propane (trimethylene glycol) with fuming HIAq at 100° (Freund, M 2, 640) Also from trimethylene bromide, alcohol, and

KI (Perkin, jun, C J 51, 12)
Di-iodo-propane CH, CL, CH, Allylene di-hydro-di todide (148°) S G 2 2 15 (O), 2 45 (S) Obtained by direct combination of allylene with HI (in conc solution) (Oppenheim, Bl [2] 4, 484, Semenoff, Bl [2] 5, 446) Heavy oil Partly decomposed by distillation, but may be distilled with steam or with any indifferent gas Sl sol alcohol, v sol ether Becomes coloured in air and light Alcoholic potash forms CH, CI CH, Ag,O gives acetone (Sorokin, Z 1871, 264)

IODO-PROPIOLIC ACID C.HIO, . s

ICCCO,H Iodo propargylic acid Iodo-acetylene carboxylic acid [140°] Small colourless prisms or glistening needles

Formation -1 By saponification of the ethyl ether -2 By the action of a solution of iodine in KI upon the cuprous compound of calcium or barium propargylate

Reactions —It combines with HBr to form brom 10do acrylic acid [96°], with HI it yields And node acrylic acid [133°], with bromine dis-solved in chloroform it yields di-brome-iodeacrylic soid [147°], with an ethereal solution of hodine, tri iodo-acrylic seid [207°], and with AMINE C13H1, IN 3 5.5 CH2I CH2 CH(NHPh), iodine bromide, bromo-di-10do acrylic acid [182°]. On the other hand, an aqueous solution of bromine converts it into di-bromo iodo ethylene

IBrC CHBr with evolution of CO2

Salts -A'K small glistening very hygroscopic needles - A'Ag white pp, decomposed by warming with water forming AgI -A'Ba easily soluble amorphous solid —A'2Cu

Ethyl et. er A'Et [68°], large colourless prisms Formed by the action of a solution of iodine in KI upon the cuprous compound of propargylic ether (Baeyer, B 18, 2274, Homolka

a. Stolz, B 18, 2282, 19, 536)
a-IODO PROPIONIC ACID C₃H₅IO₂ v e CH₃ CHI CO₂H Prepared by digesting syrupy lactic acid (1 mol) with PI₂ (1 mol), pouring the product into water and extracting with ether (Wichelhaus, A 144, 352) Oil, nearly insol water

β-Iodo-propionic acid CH,I CH, CO,H [82°] Formation -1 By the action of nodide of phosphorus on glyceric acid (Beilstein, A 120, 226, 122, 366, Erlenmeyer, A 191, 284) 2 From acrylic acid and cone HIAq (Wish-

cenus, A 166, 1)

Preparation -The product of the oxidation of glycerin with nitric acid is evaporated on the water-bath, and the syrupy residue diluted with water until it possesses S.G 126 This solution (30 cc) is then poured into a flask containing iodine of phosphorus prepared from iodine (50 g) and yellow phosphorus (65 g) After the vigorous action has taken place, the solid residue is recrystallised from water (V

Meyer, B 19, 3294, 21, 24)

Properties - Colourless laminæ, v sol hot, v sl sol cold, water, v e sol alcohol and ether May be converted into propionic acid by HI or by sodium amalgam (Moldenhauer, A 131, 328) By boiling with water it is converted into hy dracrylic acid and a little acrylic acid Boiling with water and Ag2O forms hydracrylic acid, para adıpı malıc acıd C6H10O3, dihydracrylic acid C₈H₁₀O₅, and paracrylic acid C₃H₄O₂ [69°] (Beilstein, Wislicenus, Z [2] 4, 683, Socoloff, Klimenko, Bl [2] 34, 321, v also ACRYLIC ACID) B-Iodo propionic acid is converted into adipic acid by heating with reduced silver (W) AgNO, gives in an aqueous solution of β iodo propionic acid an immediate pp of AgI

(188°) Methylether MeA' SG 11841 Colourless oil, turning (Henry, C R 100, 114) brown in light Is not pungent Formed from

the acid, alcohol, and H₂SO,

Ethyl ether EtA' (202°) (Fittig a Wolff,

A 216, 128) SG = 1707 (Henry) Formed by heating an alcoholic solution of the acid after adding a few drops of H.SO, Formed also by dissolving the acid (1 pt) in alcohol (3 pts) and saturating with HCl, the yield is only 50 pc. for much EtI is evolved (Lewkowitsch, J pr [2] 20, 167; Wichelhaus, B 1, 25, Wishcenus, A192, 129) Oil Partly decomposed on distillation

Amide CH₂I CH₂ CONH₂ [101°] Formed by the action of aqueous NH₃ on the methyl by the action of agents, ether in the cold (Henry) Colouriess tables, ether in the cold (Henry) V sol water Its solution gives a pp. with AgNO.
8-IODO PRO-IONIC ALDEHYDE

CH2I CH2 CO H S G. 15 2 21 Prepared by the action of rodine (25 g.) and rodic acid (10 g) on proprionic aldehyde (18 c c) diluted with alcohol

(50 cc) It is washed with KOH solution and poured into water (Chauta d, A Ch [6] 16, 157).

Properties -Heavy colourless liquid, not inflammable, with an exceedingly irritating vapour Miscrole with alcohol, ether, and acetone, al sol. Is totally decomposed at 100° dilute solutions of KOH, NaOH, or NH, HO attack it slowly in the cold Cone solutions resinify it Mineral acids behave similarly HNO, oxidises it to CH₂I CH₂ CO₂H [82°] forms propyl acetate (90°) AgC $Ag(C_2H_3O_2)$ AgCN and silver torms propyl accesse (30) 1861 and saves sulphocyanide give CH₂ (CN) CH₂ CO H and CH₂ (CNS) CH₂ CO H Anline gives the compound CH₂I CH CH (N^{**} C₆H₃)₂.

IODO PROPYL ALCOHOL v Iodhydrin of

PROPYLENE GLYCOL

Di 10do - propyl alcohol C,H,I,O Dr rodide of allyl alcohol CH I CHI CH,OH Prepared by dissolving iodine in allyl alcohol (Hubner a Lellmann, B 13, 460, 14, Colourless needles Easily decomposed by light or heat Sol alcohol, ether, and benz ene, insol water On heating the chloroform solution it gives a compound crystallising in colourless prisms [160°], which is probably an iodo allyl alcohol

Di 10do isopropylalcohol CH, I CH(OH) CH, I Glycerin di wdhydrin [c -18°] SG 15 24 Prepared by heating the s dichlorhydrin of glycerin with KI and water on a salt bath Nahmacher, B 5,353, Claus, A 168,24) Faintly yellowish oil Decomposes when distilled

p-IODO PROPYL-BENZENE $C_aH_4(C_2H_7)I$ [14] [250°] Formed by heating p diazo propyl benzene with HI (Louis, B 16, 110) Vola tile with steam Colourless oil Sol ether, in sol alcohol, almost insol water On oxidation with cold CrO, in acetic acid it gives piodo benzoic acid

p Iodo iso propyl benzene C₆H₄(C₃H₇)I (234°) Prepared by heating p diazo iso propyl benzene with HI (Louis, B 16, 114) Colourless oil On oxidation it gives p iodo benzoic acid

ω-IODO PROPYLENE v ALLYL IODIDE

a lodo propylene CH, CHI Cly, Allylene hydro vodude (82°) (S), (93°-103°) (O) SG 2 1835, 12 1803 Formed by decomposing di Allylene 10do propane CH3 CI2.CH3 (1 mol) with alcoholic KOH (1 mol), and mixing the distillate with water (Semenoff, Bl [2] 5, 446, Z 1865, 725, Oppenheim, Bl [2] 4, 434, Z 1865, 719)

Di iodo propylene C,H,I, 1e CH, CI CHI Allylene di vodide (198°) Obtained by expos-

ing allylene for two months to a solution of I in aqueous KI in sunshine (Oppenheim Turns brown in light Yields allylene ith alco-

holic KOAc

Tri iodo propylene CHI CI CH2I Dr rodo. allyl wodide Propargyl tri wodide [41°] Formed by the combination of propargyl iodide with iodine (Henry, B 17, 1132) Small colourless needles

Tri iode-propylene CH, CI CI. Iodo-allylene todide [64°] From silver allylene and di rodide iodine in echereal solution (Liebermann, A 135, Decomposes at 78° V e sol 273) Needles ether, m sol alcohol. Alcoholic potash gives 10do-allylene

IODO-PROPYLENE-GLYCOL v Iodhydrin of GLYCBRIN.

IODO-PROPYL-THIOPHENE C.H.IS te O₄H₂IS C₂H, From n propyl throphene (Rufer, B. 20, 1743) Oil, volatile with steam

Ita-IODO PYROTARTARIC ACID C,H,IO From itaconic acid and HI at 150° Z 1866,722) Nodules Reduced by [185°] (Swarts, Z 1866, 722) further treatment with HI to pyrotartaric acid

TETRA IODO PYRROLE C.I.NH 'Iodol' 8 02, S (90 pc alcohol) 6 at 15°, S (ether) 50 Formed by the action of an ethereal solution of iodine on pyrrole potassium (Ciamician a Dennstedt, G 13, 18, B 15, 2582), and by the action of iodine on an alkaline solution of pyrrole (Ciamician a Silber, G 16, 543, B 18, Lor; yellowish brown flat prisms or minute yellow needles (frc.n dilute alcohol) Sol ether, acetic ac d, and hot alcohol, nearly insol cold alcohol, insol water and aqueous acids Decomposes at about 140°-150° Gives a white pp with AgNO3 instantly blackening, green colouration with HgCl, Has no basic properties It is not decomposed by boiling water, but boiling HClAq blackens it It does not dissolve in aqueous kOH, but alcoholic potash dissolves it forming a potassium derivative which is decom posed by acids (even CO) but not by water Zinc dust and KOH reduce it to pyrrole (Ciami cian a Silber, B 19, 3027) When heated gently with conc H₂SO₄ it gives at first a green, then a dirty violet colouration Its alcanolic solution gives a red colour with nitric acid (Vulpius) is employed pharmaceutically as a substitute for iodoform for suppurating sores, fungoid growths, hay fever, &c, having the advantage of possess ing no odour, and exerting no poisonous effect upon the system

[63°] (above IODO-QUINOLINE C.H.IN 300) SG 193 Prepared by heating quinoline with a KI solution of iodine and HIO, (La Coste, B 19, 780) Monoclinic prisms, or long thin needles I asily volatile with steam

Salts -B'HCl 1aq small yellow needles -B',H PtCl, 2aq long orange needles, sl sol water -B H C1,0, sparingly soluble yellow needles or plates

Methylo rodide B MeI glistening golden plates, sol hot water v sl sol cold water and alcohol, insol ether

Methylo chloride B'MeCl aq fine yellowish needles or thick yellow prisms, dimorphous (Lehmann, Z K 12, 377), v sol water -(B'MeCl) PtCl fine orange crystals, sl sol cold water

Formed by heating $(Py\ 3)$ chloro quinoline with HI (Friedlander a Weinberg, $B\ 18,\ 1531)$ White needles SI sol water, $v\ sol$ other sol vents - BHI long needles -B',H,Cl,PtCl, aq red needles

[90° uncor] Di-iodo-quinoline CaH, IaN Formed by the action of sodine in CS, on quino line (Claus a Istel, B 15, 824), Dull-green metallic needles Sol alcohol, ether, and acetic acid

DI IODO-QUINONE C.H.I.O. [159°] Formed by the action of todic acid on the discetyl derivative of hydroquinone (Metzler, B 21, 2555) Yellow needles (from alcohol) Is converted by

the action of sulphurous acid into the hydroquinone [142°]

Di 10²0 quinone C₂H₂I₂O₂ [3 5 4 1] [180^o] From di-10do p amido-pheno! (q v), H₂SO₄ and K₂Cr₂O₂ (Seiffert, J pr [2] 28, 438) Formed also by exidising di 10do phenol sulphonic acid with CrO_s (Kehrmann, J pr [2] 37, 336) Golden plates (from benzoline) Readily sublimes, almost insol cold, v sl sol boiling, water With HCl and SnCl, it gives di iodo hydroquinone [145°]. FeCl, reconverts this into di-iodo quinone

Di iodo quinone chlorimide CaH2I2 From C, H2I2(NH2)(OH), hydric chloride, and bleaching powder solution (Seiffert, J pr [2] With NMe, Ph it gives 28, 438)

C_sH₂I₂<0>C_sH₁NMe₂ IODO RESORCIN C_sH₃IO₂ 16 C_sH₃I(OH), [67°] Formed by agitating an ethereal solution containing resorcin (10 pts) and iodine (24 pts) with PbO (110 pts), distilling off the ether and recrystallising from benzene (Stenhouse, C N 26, 279, A 171, 311). Trimetric prisms, sol. water

Tri iodo resorcin C,HI,(OH).. [145°] (M a. N), [154°] (C) Formed, together with a brown substance insoluble in CS2, when ICl is added to an aqueous solution of resorcin (Michael a. Norton, B 9, 1752) Formed also by adding an aqueous solution of resorcin to a solution of KIO., iodine, and KI (Classen, B 11, 1443). Prepared by adding bleaching powder to a dilute alkaline solution of resorcin (1 mol) and KI (7 mols), and then acidifying (Degener, J pr [2] 20, 324) Needles (from CS₂), al sol hot water, v sol alcohol and ether May be sublimed. Boiling HNO, gives tri nitro resorcin

Di acetyl derivative C.HI.(OAc)... [170°] Needles, v sol alcohol and ether

IODO RESORCIN SULPHONIC ACID $C_6H_2I(OH)_2(SO_3H)$ From potassium resorcin sulphonate and iodine (H Fischer, M 2, 340) kA' 3aq minute crystals

Iodo resorcin disulphonic acid

C_eHI(OH)₂(SO₂H)₂. Formed by digesting potas sium resolution disulphonate (30 g) with iodine (33 g) in dilute alcoholic solution at 100° (F) long needles

IODO SALICYLIC ACID v IODO O OXY-BENZOIO

10D0 STEARIC ACID C14H35IOr. From di oxy stearic acid and HI (A Saytzeff, J pr [2] 33, 309) Oil

Iodo stearic acid C, H, IO. From oleic acid, PI., and a little water The product is mixed with water and extracted with ether (M C a A Saytzeff, J pr [2] 35, 384)

Properties - Oil Resembles the preceding acid

Reactions -1 Reduced by Zn and HCl to stearic acid -2 Moist Ag₂O forms a substance that is unsaturated (taking up 55 pc I from its solution in HgCl₂Aq), but is converted by alcoholic KOH into oxy steams acid -3 Alcoholic KOH forms solid iso oleic acid [45°], and also ordinary oleïc acid

Iodo-stearic acid C18H351O2. Formed by heating iso cleic acid with tri iodide of phosphorus and water (Coust a Saytzeff, J pr [2] 37, 276, Bl. [2] 47, 169) Oil, sol ether.

Reactions -1. Yields an oxy stearic acid [85°] on treating with silver oxide —2 Alcoholic potash regenerates iso-cleic acid [40°-45°], but forms no cleic acid —8 Alkaline KMnO₄ oxidises it to di-oxy-stearic acid [78°]

10D0-STEARIDENIC ACID C18H33IO2 Iodooletc acid From ricinoleic acid O18H24O3, water, **P**, and 10dine at 100° (Claus, B 9, 1917) Oil Reduced by boiling with zinc and HClAq to steam acid Combines with bromine

DI-IODO-SUCCINAMIC ACID

CO.H CH, CI. CONH, Ethylether A'Et Ethylether A'Et [134°], long needles, alightly soluble in cold water Formed by the action of iodine upon diazo succinamic ether CO₂Et CH₂ CN₂ CONH, in ethereal solution (Curtius a Koch, B 19, 2462, J pr [2] 38, 485)

IODO-TARCONINE v NARCOTINE IODO-THIENYL METHYL KETONE

[129°] Iodo-acetothienone CASHAI CO CH. Formed by the action of acetyl chloride upon mono- or di iodo thiophene in presence of Al₂Cl₆ (Gattermann a Römer, B 19, 692) Long colourless needles (from alcohol) Very volatile with steam Strong odour By alkaline KMnO it is oxidised to iodo thiophene carboxylic acid [131°]

Phonyl hydraside C, SH2I C(N, HPh) CH, [184°], yellow tables, al sol alcohol

(a) IODO-THIOPHENE C.H.IS & 6

CH CH. S (182° cor). Oil Formed by the

CH CI action of iodine and HgO on thiophene at the ordinary temperature (Meyer a Kreis, B 17, 1558, Egli, B 18, 544) With sodium and EtI it gives ethyl thiophene With Na and n butyl bromide it forms n-butyl thiophene (182) Gives an iodo-nitro thiophene [74°] (Kreis, B 17, 2073)

Di-10do-th10phene C4H2I2S [404°] crystals Formed by the action of 2 mols of 10dine and HgO on thiophene at the ordinary temperature (Meyer a Kreis, B 17, 1558)

IODO-THIOPHENE CARBOXYLIC ACID C₄SH₂I(CO₂H) Iodo throphenic acid [131°] Formed by oxidation of iodo threnyl methyl ketone with alkaline KMnO, (Gattermann a Römer, B 19, 693) Colourless silky needles (from water) Sublimes in glistening tables — NHA' needles, sl sol cold water

(a) - IODO-THIOPHENE -(B) -DI BULPHONIC ACID C.HIS(SO.H). Formed by sulphonation of (a)-10do thiophene On reduction with sodium smalgam it yields thiophene (β) di sulphonic acid (Langer, B 18, 559)

IODO-THIOXENE 18 IODO DI METHYL THIO-PHENE (q v)

IODO - THYMOL C.H.MePr(OH)I [1436] Prepared by adding rodine (85g) to a solution of thymol (5g) in ammonia (6 cc) mixed with alcohol (2 cc) and distilling the oily product with steam (Willgerodt a Kornblum, J pr [2] 39, 289) Lustrous white needles, insol water, sol other solvents. Oxidized by Man and H SO dised by MnO, and H, SO, or by FeCl, to thymo-quinone Not attacked by aqueous KOH at 800° HNO, forms nitro thymol, displacing I by NO, H₂SO, forms a sulphonic acid.

Ethylderivative C.H.MoPrI(OEt) [520] Opaque white rimetric tables, insol cold water, al sol hot water and alcohol

Acetyl derivative C_cH₂MePrI(OAc) White needles

Bensoyl derivative C₆H₂MePrI(OBz). [95°] Large tables

Prcryl derivative [155°], yellowish crystalline aggregates

IODO THYMOL SULTHONIC ACID

C.HMePr(OH)ISO,H [1 4 3 2 6] From thymol by successive sulphonation and iodation (Kehrmarn, J pr [2] 39, 392) Gives an iodo thymo quinone on oxidation HNO, gives di nitro quinone on oxidation HNO, gives di nitro thymol [53°] —KA'2aq crystals melting in water of crystallisation at 80°, decomposed at

120° -BaA'2-AgA' 10D0 - THYMOQUINONE C.HMePrIO, [5 2 6 4 1] [61°] Formed by oxidising 1.dothymol sulphonic acid with CrO, (Kehrmann, J pr [2] 39, 392) Yellowish red prisms duces to an iodo hydrothymoquinone [74°

Oxim C_sHMePrIO(NOH) [5 2 6 4 1] [130°] Formed by heating the quinone with hydroxylamine hydrochloride in diluted (75 p c) alcoholic Long yellow prisms and needles, sol alcohol and ether, insol cold water Its acetyl derivative C.HMePrIO(NOAc) crystallises in golden needles [70°] Its sodium derivative crystallises ir greenish laminæ

Iodo thymoquinone CaHMePrIO, [5 2 3 4 1] From 10do carvacrol sulphonic acid by oxidation with chromic acid mixture (Kehrmann, J pr [2] 40, 188) Garnet red tables, sol alco hol and ether More volatile with steam than Smells like quinone Hydroxyl its isomeride amine slowly forms an oxini

o IODO TOLUENE C,H,I 16 C,H,I CH, [21] (205°) (B a K), (211° 1 V) (K) S.G 201697 (B a K) Formed from o toluidine by the diazo reaction (Beilstein a Kuhlberg, Z 8, 102, A 158, 347, Kekulé, B 7, 1007, Mabery a Robinson, Am 4, 101) Oil

Reactions -1 Oxidised by dilute nitric acid to o iodo benzoic acid [157°] -2 With CICO Et and Na it forms C.H.Me CO.Et -3 Cro.Cl. gives C.H.I CHCl, and a little C.H.I CHO (Stuart a Elliott, C J = 53,805) -4 When heated with H₂SO₄ it forms iodo toluene sulphonic acid, di 10do toluene, and tri 10do toluene (Neumann, A. 241, 62)

m Iodo toluene CaH, I CH, [81] SG 20 1 698 From m toluidine by the diazo

reaction (B a K) o Iodo-toluene C.H.ICH, [41]

(211 5°) From p toluidine by the diago- reaction (Körner, Bull Acad Belg 1867, 157) The same body appears to be formed from mercury ditolyl and iodine, although the melting point is given as 20° (Dreher a Otto, A 154, 171) Laminæ May be sublimed Gives p iodo benzoic acid when oxidised by chromic acid mixture H₂SO₄ forms iodo-toluene sulphonic acid and di- and tri-iodo-toluene (Neumann, A. 241, 58)

-lodo-toluene v BENZYL 10DIDE. o-IODO TOLUENE BULPHONIC ACID C,H,ISO, &c CH, C,H,ISO,H From o-todotoluene and SO₂ (Mabery & Palmer, Am 6, 170) Syrupy liquid —BaA'₂1½ aq : needles.—CaA'₂2½aq —PbA'₂2aq

p-Iedo-toluene (a)-sulphonic acid CH, CaH, I SO₂H Formed, together with the (β) isomeride, by gracually adding p iodo toluene to SO, both dissolved in chloroform (Glassier, B 8,560) - BaA'2 4aq needles, v e sol. water

p Iodo toluene (β)-sulphonic acid

CH, C,H,I SO,H Formed as above Deliquescent crystalline mass - KA'aq very soluble laminæ -NaA' aq dense aggregates of whetstone shaped very soluble cystals - CaA', 3aq very soluble silky needles - 3aA', aq thin lamınæ, al sol water - GuA', 6aq light blue needles, v sol water

Amide C.H.MeI SO,NH. [179°] Crystals, m. sol hot water, v so alcohol

Iodo-toluene disulphonic acid

 C_{u} - I_{2} MeI(SO₃H). [1 4 3 x]

From C₄H₂Me(NH₂)(SO₂H)₂ by diazo- reaction (E. Richter, A. 230, 325, Limpricht, B. 18, 2170) Slender white needles, v sol alcohol and water -BaA"6aq prisms, v sol water -

K,A"2aq small prisms
Chloride C,H2McI(SOCl), [143°] After one fusion it melts at 126° Long white prisms,

sl sol ethe-

Amide [130°-132°] White needles (from water'

•IODO-o-TOLUIDINE C_uH₁MeI(NH₂) [1 4 2] [49°] (273°) From 10do o nitro toluidine by reduction (Heynemann, Z [2] 6, 402, A 158, 338) Needles Boils, with rapid decomposition, at 273° V e sol alcohol, ether, and CS, B'HNO, colourless nacreous laminæ S 95 at

Iodo-toluidine C₄H₂MeI(NH) [143] [189°] From p 10do toluene by nitration and reduction (Glassner, B 8, 561) Needles or plates, v sol alcohol -B'HCl needles -B'HNO, plates -B'H,SO, needles

Di-10do-p-toluidine C_eH.MeI₂(NH₂) [1 3 5 4] [124 5°] Formed by the action of ICl on p tolu idine dissolved in HClAq (Michael a Norton, B 11, 115, Am 1, 263) Ramified groups of slender needles, m sol cold alcohol, sl sol hot water IODO-TOLUIDINE SULPHONIC ACID

C_aH₂Me(NH)I(SO₃H) [1 2 4 5] From the diazo derivative of C.H.Me(NO,)(NH,)(SO,H) [1 2 4 5] and cone HI at 140° (Limpricht a Foth A 230, 308, B 18, 2185) Satiny needles (containing aq) Sl sol cold water, m sol hot water — BaA'₂" trimetric tables, v sol water

IODO-TOLUQUINONE C.H. MeIO, [6 2 4 1] [117°] Formed by oxidising a solution of iodo cresol sulphonic acid in sulphuric acid with chromic acid (Kehrmann, J pr [2] 37, 340, 39, 392) Long reddish yellow needles, m sol ether Reduced by stannous chloride to iodo hydrotoluquinone [111°] With hydroxylamine it gives the mono-oxim crystallising in short yellow prisms [156°]

Di-iodo-toluquinone C.H Mel.O. [36241] From di iodo m cresol sulphonic acid and CrO, (Kehr nann, J pr [2] 39, 392) Garnetred lamina, v sol organic solvents May be sublimed

DI-IODO-DITOLYL [3 4 1] C.H.MeI C.H.MeI [1-8 4] [100°]. From di amido ditolyl by Sandmeyer's modification of the diazo-reaction (Stolle, B. 21, 1096) Yellow needles

-- IODO - DI - TOLYL - ETHYLIDENE - DI -

heating 10do acetic aldehyde with p-toluidine (Chautard, A Ch [6] 16, 156) Orange yellow prisms or tables, decomposed by heat not furnish crystalline salts

IODO TOLÝL METHYL KETONE

C.H.Mel CO CH, [1 2 5] [39°] Formed by heating diazo tolyl methyl ketone (from amidotolyl methyl ketone [102°]) with an excess of HI (Klingel, B 18, 2700) Yellowish prisms V sol alcohol and ether, sl sol ligroïn and benzene, insol water By CrO, it is oxidised to

benzene, insol water 10do iso phthalic acid [204°]

\$\beta \text{IODO-VALERIC ACID C_H_IO_1e} \text{Solidines at 59°} \text{Solidines at 59°} Separates as crystals when HI is passed into a concentrated solution of \$\beta\$ oxy isovaleric acid (Schirokoff, J pr [2] 23, 285) Converted by

sodium amalgam to isovaleric acid

Iodo valeric acid CEtMeI CO,H (?) Hydronodide of tiglic acid [865°] Formed by the combination of tiglic (methyl crotonic) acid with HI which may be effected in the cold (Schmidt a Berendes, A 191, 117) Formed also, together with the following, when angelic acid is heated with HIAq (Schmidt, A 208, 254) Needles, sl. sol cold water, decomposed by boiling with water Converted by zinc and dilute H.SO, into CEtMeH CO,H Aqueous AgNO, gives AgI, tiglic acid and CO2.

Iodo valeric acid CH, CHI CHMe CO,H [46°] Hydro iodule of angelic acid From angelic acid and cone HIAq in the cold (Fittig, A 216, 162) Prisms, v sol water Zino and dilute H.SO, converts it into CEtMeH CO.H. Aqueous Ag O, gives AgI, tiglic acid, and CO. Aqueous Na,CO₃ at 0° gives CO₂, ψ butylene CH₂ CH CH CH₃, and HI V also Americ acid, vol 1 p 266

IODO-ISOVALERIC-ALDEHYDE C,H,IO ...

(CH,),CH CHI CHO (?) SG 17 2 17

Preparation - Isovaleric aldehyde (24 c.c) dissolved in alcohol (50 cc) is treated with iodine (20 g), and iodic acid (8 g) The reaction takes place at the ordinary temperature, and is complete in about 15 days. The liquid is poured into excess of water, and decolourised by alkali or reduced silver (Chautard A Ch [6] 16, 160).

Properties - Colourless liquid, blackening on exposure to light, and having an extremely irritating and suffocating odour It is completely decomposed at 100°, and is not solidified at - ?0° V sol alcohol and ether, less sol benz-

ene, CHCl, and CS Sl sol water

Reactions -Rapidly decomposed by alkalis. The action of ammonia is complex, giving valerie aldehyde ammonia, valeridine CieHi,N, and valeritrine C14H2-N Forms a crystalline compound with NaHSO, Ag(C2H2O2) at 100° yields amyl acetate (138°) AgCN and AgSCN react forming AgI and the corresponding derivatives. Forms a mono- and a di anilide with aniline.

IODO-VANILLIN v Methyl derivative of

IODO-DI OXY-BENZOIC ALDEHYDE

DI-IODO-VINYL-AMINECI, CH(NH2) [192° with decomposition] Formed by the action of cold aqueous NH₃, CO₂ and alcohol being eliminated upon the di iodo oxy acrylic ether CI, C(OH) CO, Et, obtained by treating diazooxy acrylic ether CN2.C(OH) CO2Et with an ethereal solution of nodine (Buchner a. Curtius, AMINE CH.LCH(NHC,H,Me),. Obtained by B. 19, 851) Small yellowish prisms. Very sparingly soluble in cold water and ether, more easily in hot water and hot alcohol Volatile with steam It is stable towards acids, but alkalis set free NH₃ in the cold

DI-w-IODO-o-XYLENE C₆H₄(CH₂I)₂, o-Xylyl ens-todide [110°] Prismatic crystals Formed by heating phthalyl alcohol (di ω oxy-xylene)

with HI (Leser, B 17, 1826)

Di-w-lodo p-zylene C₆H₄(CH₂I)₂ [c 170°]

Obtained by boiling [4 1] C₆H₄(CH₂OH)₂ with cone HIAq for a few minutes (Grimaux, Z 1870, Slender needles, sl sol ether, v sol boiling alcohol and chloroform Turns yellow in air Not very volatile with steam

IODOPLUMBIC ACID H.PbI., v LEAD,

todide of, Combinations, No 3

IONS. The elements or radicles into which a compound is primarily separated by electro lysis (v Physical methods, section Electrical

methods)

IPECUANIC ACID C, H, O, An acid exist ing, according to Willigk (A 76, 342), along with emetine (q v) in the root of Cephalis Ipecacu anha It is extracted by boiling alcohol, ppd. by basic lead acetate, and the pp decomposed by H.S Reddish brown, very bitter, amorphous mass, m sol ether, v sol alcohol and water Colours ferric salts green, the colour being changed to violet by ammonia Its dilute solu tion does not ppt Pb(OAc), but ppts basic lead acetate Its alkaline solution absorbs oxygen from the air It thus somewhat resembles gallic acid Podwyszotzky (Ph [3] 10, 642) by extracting specacuanha with ether and light petroleum obtained an acid ('Erythrocephalein'), which formed a purple red alkaline salt, and which crystallised from chloroform in coloured needles

IPOMIC ACID $C_6H_{10}O_4$ [104°] Produced by the action of nitric acid on jalapin (Mayer, A 83, 143, Poleck a Samelson, C C 1884, 813)

Resembles sebacic acid

IRIDIUM Ir At w 1925 Mol w un known [2200°] (Van der Weyde), [1950°] (Volle, C R 89, 702), [2500°] (Pictet, C R 88, 1317) S G 22 42 at 17 5° (Deville a Debray, P M [4] 50, 651) S H 0°-100° = 0323, 0°-1400° = 0401 (Violle, C R 89, 702) C E linear 000007 (Fizeau, C R 68, 1125)

Occurrence -As metal, alloyed with Pt, Os, Ru, Rh, and Pd Specimens of platin iridium, osm iridium, &c, contain from 25 to 78 p c. Ir (v Deville a Debray, A Ch [3] 56, 431, Berzehus, P 13, 435, 527, 15, 208) In 1802 Tennant (T 1804 411) noticed a metallic residue when he dissolved Pt ore in aqua regia, this residue was examined by Descotils (Gehlen's Journ Chem 2,273), and Fourcroya Vauquelin (Gehlen's Journ Chem 3, 362) In 1804 Tennant (lc) showed that the residue contained two new metals, to one he gave the name Iridium be cause of the varied colours of its oxides, and to the other the name Osmium because of the peculiar smell of its volatile oxide

Formation —1 By digesting Ir₂O₂ or IrCl₂ with ormic acid —2 By action of sunlight on an alcoholic solution of Ir sulphate

Preparation - When Pt ore is heated with aqua regia osm iridium and platin-iridium remain

Schneider (A. Suppl 5, 261) mixes the insoluble in aque regia with N.Cl, and heats to low redness in a stream of Cl, Os 3 thus removed The residual mixed chlorides are triturated with the smallest possible quantity of water, and then washed on to a filter, the solution is treated with Cl, mixed with a little HClAq, and shaken up with excess of KCl, the pp is washed with water, and then with saturated KClAq The pp is now nearly pure K, MCl, M=Tr, Ru, and Pt The pp is dissolved in much foiling water, and H is passed in for several days (the flask being closed by a caoutchouc cork) until the supernatant olivegreen liquid treated with potash becomes colour less and then blue or turbid Pt and Ru are thus wholly ppd as metals, and most of the Ir remains in solution as IrCl, His removed by a stream of CO,—otherwise explosions occur on opening the flask from the action of the ppd Pt and Ru on the H and O in the flask-the cork is removed, and the liquid is again saturated with H, Ir is ppd on the surface of the liquid in large lustrous laminæ -2 Matthey (Pr 28, 463) prepares Ir free from all metals except Pt as follows Ordinary Ir, finely divided, is fused with 10 times its weight of Pb, the Pb s dis solved in HNO, Aq, and the insoluble is digested for a long time with aqua regia, the insoluble is fused with kHSO₄ (to remove Rh), and then melted with 10 times its weight of KOH and 3 times its weight of KNO, in a gold crucible, the cold mass is treated with cold water, in which K iridate remains insoluble. The insoluble is well washed with water containing a little KOH and NaClO, and then with water, fairly conc cold NaClOAq is added to the residual blue solid . after a time the water is distilled off, the residue is again fused with KNO, and KOH, and treatment with dilute NaClOAq and KOHAq is re-The blue solid is now dissolved in aqua regia, the liquid is evaporated to dryness, and the residue is redissolved and filtered, the darkcoloured liquid is slowly poured into conc NaOHAq containing NaClO, and Cl is passed in, the liquid being kept in a distilling apparatus, the blue oxide of Ir thus obtained is collected, washed, dried, and reduced in a mixture of CO and CO2 (made by gently warming oxalic acid with sulphuric acid) Metallic Ir is thus ob tained, while any Fe present remains as oxide The mass is heated to redness with KHSO, and repeatedly washed with ClAq to remove Au, and with HFAq to remove SiO2, it is finally washed with water and dried Pt may be removed by dissolving in aqua regia, saturating wit i NH,Cl, dissolving the double NH, Ir and NH, Pt chlor ides in hot water, reducing by SO, when IrCl, 3NH,Cl is formed, and dissolves with olive green colour, while PtCl, 2NH,Cl remains in soluble, the reduction should be stopped before the whole of the IrCl, 2NH, Cl is reduced (the presence of a little of this salt gives a deep red colour to the mixed chlorides) The solution is oxidised by HNO,, NH, Cl is added, and the ppd IrCl, 2NH, Cl is washed with NH,ClAq, and strongly heated, when Ir remains as a grey metallic powder (Claus, J pr 42, 251) Wöhler a Muckle (A. 104, 368) reduce the mixed Pt NH, and Ir NH, chlorides by digesting with slightly warm KCNAq as black insoluble scales Ir is prepared from | till the undissolved is light vellow brown, taking the residue by various methods 1 W von care to avoid excess, IrCl, 3NH, Cl is formed and

dissolves, while PtCl, 2NH,Cl remains unreduced and insoluble For other methods of preparing Ir v Deville a Debray (A Ch [3] 56, 481), Claus (C C 1862 129), Wöhler (P 31, 161, 104, 363; 107, 357), Fremy (A Ch [8] 44, 385), Martius (A 107, 360), Bunsen (A 146, 274),

Properties -- As prepared by heating IrCl, 2NH, Cl, Ir forms a grey spongy mass, Ir as a grey powder is produced by heating IrCl, 2KCl with excess of Na, CO,, washing and reducing in H, by heat ng to whiteness and compressing, a compact lustrous mass is obtained When fused in a very powerful O H flame, Ir forms a white, lustrous mass resembling polished steel, brittle when cold, somewhat malicable at red heat (D a D) Harder than iron porous Ir varies from 16 to 19 Ir which has been very strongly heated is insoluble in all acids, Ir black is sol in aqua regia. Heated in Cl, Ir black forms IrCl.

The atomic wt of Ir has been determined by heating IrCl, 2kCl in H (Berzelius, P 13, 435, 527, 15, 208), by reducing IrCl, 2NH,Cl in H and weighing the residual Ir, and by reducing the double '- K chloride in H and dissolving out the KCl (Seubert, B 11, 1767) As no com pound of Ir has been gasified, the valency of the atom of Ir in gaseous molecules is not determined From the crystalline form of osm iridium G Rose (P 77, 143) concluded that Os and Ir are 180 morphous, and that both belong to the hexagonal system

In its chemical reactions, Ir is closely re lated to Os and Pt, and less closely but very distinctly related to Ru, Rh, and Pd, all these elements are metallic, but the instability of their salts, the solubility of the hydrated oxides MO. in alkalis, and the formation of acids H2MCl, and H, MBr, show the non metallic tendencies of the Pt metals (v Noble Metals)

Ir is used alloyed with Pt for making instru ments, &c, which remain unchanged in air, eq for making the normal metre preserved as the standard of reference Stylographic pens are sometimes tipped with Ir When Ir powder is heated to whiteness with 1 its weight of P the whole melts, on cooling, the mass may be readily | (simplest formula worked, by strongly hesting with lime, the P is

entirely removed

Reactions and Combinations -1 Heated in oxygen, compact Ir is not oxidised, Ir black is oxidised to Ir,O, which decomposes again at c 1000° (Deville a Debray, C R 1878 441, cf Dissociation, vol 11 p 397) -2 Ir black 18 oxidised by fusion with nitre, potash, potassium carbonate, or potassium hydrogen sulphate -8 Heated in chlorine IrCl, is formed, mixed with NaCl or KCl, and heated in Cl, soluble IrCl, 2Na(K)Cl is formed 4 Heated in an alcohol flame, Ir becomes covered with a black ish layer which disappears on heating in air, leaving a portion of the Ir combined with C (t IRIDIUM CARBID") -5 Ir probably combines with phosphorus when the elements are heated together, when the product is heated in air, Ir and a phosphate of Ir ere formed

Iridium, alloys of Faraday a Stodart (A Ch. 21, 73), Deville a Debray (C R 81, 839), Fineau (C R 78, 1205), Morin (C R 78, 1502),

Wöhler (A 146, 875)

Osmsum-sredsum alloy

America, California, Australia, Ural Mountains, Hexagonal prisms, lustrous, steel grey Slightly malleable, S G 19 3 to 21 1 Analyses show composition approximating to formulæ Ir Os, Ir Os and Ir Os, with Ir more or less replaced by Pt, Rh, and Ru, but it is probably non homogeneous (D a D) Heated in air, OsC, is given off, heated with KNO, and KOH K osmate and iridate are formed scarcely acted on by aqua regia Alloys with Fe (F)

Platinum iridium alloy Occurs native in octahedra 1 pt Ir heated in O H flame with 10 pts Pt gives a ductile alloy, Pt alloyed with 15-20 pc Ir is insoluble in aqua regia For accounts of the Pt-Ir alloy used for making the normal standard metre v D a D and also M Alloys of Ir with Pt and Rh, and with Pt, Rh, and Sn were prepared by D a D Alloys of Ir with Cu, Au, Pb, Hg, Ru, and Sn have been prepared

Iridium, ammonio salts of, or Irid am monium salts (Ammoniacal iridium bases) IrCl₂ dissolves in (NH₄)₂CO₂Aq and on neutralis ing with HClAq, the compound IrCl_2NH₃ is produced, treated with H₄SO₄Aq, this compound yields IrSO₄ 2NH₄ IrCl₂ 2NH₃ dissolves in boil ing NH, Aq, and the compound IrCl, 4NH, forms on cooling, this compound gives a sulphate and nitrate, SO, and 2NO, replacing Cl. From IrCl, 3NH, Cl is obtained IrCl, 5NH,, and this again yields a basic hydroxide Ir(OH), 5NH,, a carbonate Ir₂(CO₃), 10NH₃, and other salts Finally by treating IrCl, 2NH, with conc HNO, Aq the compound IrCl2(NO1), 4NH, is obtained, AgNO, Aq does not ppt Cl from this salt, treated with HClAq the salt IrCl, Cl, 4NH, is produced from which AgNO, Aq ppts only half the Cl The foregoing compounds may be formulated as double salts of IrCl2, IrCl3, IrCl4, &c , with NH3, but many of their reactions are better explained if we regard them as salts of condensed ammo niums containing Ir The following classifica tion is that usually adopted

1 IRIDOSAMMONIUM COMPOUNDS NH. Ir XI, and N,H₁₂Ir X¹₂, or NH (NH₄)Ir X₂, N₂H₄(NH₄)₂Ir \2, &c, obtained from IrCl.

Iridosammonium chloride N.H.Ir Cl IrCl_2NH3 = di-ammonioiridium dichloride) A yellow, curdy pp, ob tained by dissolving IrCl, in excess of (NH,),CO,Aq and neutralising the greenish yellow liquid with HClAq Insol hot and cold Heated gives NH,Cl, HCl and Ir (Skoblikoff, A 84, 275) Heated with H2SO, Aq, easily soluble orange coloured undosammonium sulphate, N.H. Ir SO., is produced

Iridoso diammonium chloride NaH12Ir Cl2 or N2H4(NH4).Ir Cl2 (simplest formula IrCl2 4NH, = tetrammonio iridium dichloride) IrCl, 2\H, is boiled with NH, Aq until almost all dissolved, the solution is filtered and allowed to cool Nearly white pp, insol in cold water, heated, or placed in boiling water, goes to IrCl. 2NH. (Skoblikoff, lc) The sulphate, N, H12Ir SO4, 18 obtained by the action of H.SO.Aq on the chloride, and the nitrate, N.H., Ir (NO1), by addition of Ba2NO, Aq to a solution of the sulphate in warm water

· 2 IRIDO AMMONIUM COMPOUNDS N10H20Ir2 XI or N.H.(NH4), Ir, XI, obtained from IrCl, Irido pentammonium chloride N. H. Ir. Cl. Occurs in South (simplest formula Ir.Cl. 10NH, = decammonioeridium trichloride) IrCl, 3NH,Cl is dissolved in water, an equal volume of conc NH,Aq is added, a flask is quite filled with the liquid, and allowed to stand for several weeks in a warm place until the olive green colour of the liquid has changed to deep rose red, after gentle warming, to remove excess of NH, the liquid is saturated with HClAq and evaporated to cryness, the greenish yellow salt which separates during evaporation is washed with cold water, and then crystallised from water accidited with HCl Flesh-coloured, crystalline, powder, v sl sol water (Claus, J pr 63, 99, A 98, 317)

Irido pentammonium hydroxide
N₁₀H₂₀Ir₂ (OH)₆ Known only in solution which
is obtained by digesting the chloride with moist
Ag₂O Solution is alkaline, neutralised by acids
gives carbonate, nitrate, and sulphate

8 IRIDI AMMONIUM COMPOUNDS $N_4H_{12}IrCl_2X^1_2$ or $N_2H_4(NH_4)_2Cl_2.IrX^1_2$, obtained from series 1

by oxidation.

Indi-diammonium chloride? better chlorırıdı - dıammonıum chloride N₄H₁₂IrCl₂Cl₂ IrCl, 4NH, = tetrammonio (simplest formula warming iridosammonium chloride (N₂H₈Ir Cl₂) with cone HNO, Aq, dissolving the salt which separates in hot water, adding excess of HClAq, and crystallising from hot water Violet octahedra, AgNO, Aq ppts only the Cl from this salt. The salt which separates after treating N2H6Ir Cl2 with HNO_s is the N₄H₁₂IrCl₂ (NO₃)₂, AgNO Aq does not ppt Cl from this salt When this salt is evaporated with dilute H2SO, Aq, the sulphate, N4H, IrCl, SO, is obtained (Skoblikoff, Ic) Palmaer (B 22, 15) describes N₂H_{1,3}Ir Cl Cl₂, N₂H_{1,3}IrCl SO, 2H₂O, N₂H_{1,4}IrCl (NO₂), N₂H_{1,2}IrCl₂Cl, and N₂H_{1,2}IrCl (NO₂)₂, N₄I (N₄H_{1,2}IrCl₂)₂SO₄ 2H₂O

References — For other memours besides those referred to, v Weltzien, A 97, 19, Gibbs a Genth, J 1858 214, Birnbaum, B 12, 1544

Iridium, boride of When Ir is heated with B to a very high temperature a fusible mass is obtained, no definite boride has been isolated (Wöhler a Deville, A Ch [3] 52, 71)

Iridium, bromides of (Birnbaum, A 133,161) Only one bromide has been isolated, IrBr, 4H,O, there are indications of the existence in solution of a tetrabromide, IrBr, Ir does not combine directly with Br, nor is it soluble in a mixture

of HNO, and HBrAq

IRIDIUM TRIBROMIDE IrBr, 4H.O (Iridobromide Iridium sesquibromide) When the blue hydrate IrO,H, (obtained by heating a solution of IrCl, with alkali) is dissolved in HBrAq and evaporated in vacuo, olive green six-sided crystals separate, and then steel blue needles. The olive-green crystals are IrBr, 4H₂O, and the steel-blue crystals are IrBr, 3HBr 3H₂O. The bromide loses 3H₂O at 100°-120°, it is sol water, insol alcohol or ether, aqueous solution is green, but becomes blue probably with formation of IrBr.

Irndo-bromhydruc acid Irng, $3H_0O$ Crystallises in steel-blue crystals which melt at 100° , giving off $8H_0O$, deliquescent, easily sol water, alcohol, ether, oxidised by HNO_3 , probably to Irng

Ammonium-viridium tribromide, or Ammonium widobromide or bromiridite

2(IrBr, 8NH,Br) 8H,O, is obtained by reducing IrBr, 2NH,Br (forme.1 by adding IrCl, 2NH,Cl to hot NaBrAn and cooling' by SO, and neutralising by (NH,)2CO. The following other double salts are described by Birnbaum (A 133, 161) IrBr,3HgBr, IrBr, 3AgBr, IrBr, 3KBr 8H,O, IrBr, 3NaBr 12H,O

IRIDIUM TETRABROMIDE (Iridibromide) When IrO, H, is dissolved in HBrAq, or when IrBr, 2KBr is decomposed by H,2SiF,Aq, a solution is obtained which loses Br on evaporation, and on addition of HNO,Aq, efter evaporation, gives a deliquescent, blue, crystalline mass, easily sol in water and alcohol The blue solution probably contains IBr, 2HBr (Birnbaum) This solution does not yield double compounds with other metallic bromides

Ammonium viriavium tetrabromide, or Ammonium viriavbromide or brominidate IrBr₄3NH₄Br ((NH₄)₂IrBr₈) Dark blue octahedra, by adding IrCl₄2NH₄Cl to hot NaBrAq, and cooling

Potassium bromiridats IrBr, 2KBr(K, IrBr,) When solution of IrCl, or IrCl, 2NaCl, or IrCl, 2NH,Cl is warmed with con KBrAq, a greenish blue liquid is obtained from which very

greenish blue liquid is obtained from which very dark blue crystals of K₂IrBr_s separate, the salt is recrystallised from hot water Sodium bromridate also exists

Iridium, carbide of (? IrC.) When a coherent mass of Ir is held in the flame of a spirit lamp, black masses appear on the surface, these burn when heated in air and leave 80 2 pc Ir (Berzelius, P 15, 213)

Iridium, chlorides of Three chlorides are known IrCl₂, IrCl₃, and IrCl₄, as none has been gashed the formulæ are not necessarily molecular (v. Iridium, haloid compounds of) When Ir black is heated in Cl. IrCl₃ is formed, when Cl is passed over a heated mixture of Ir black and KCl, IrCl₄ 2KCl is produced

IRIDIUM DICHLORIDE (Iridosochloride) IrCl, A blackish green, insoluble, solid By passing Clover Ir black heated to low redness (Berzelius, P 13, 470) The change is not complete, as the temperatures of formation and uecomposition are nearly the same (Claus, A 59, 219) By heating Ir sulphite in Cl (Fellenberg, P 50, 66) By carefully heating IrCl, (Skoblikoff, A 84, 275) Seubert (B 11, 1761) describes an acid IrCl, H₂SO₂ 4NH₄Cl from which salts of NH₄ and Na are obtained

IRIDIUM TRICHLORIDE (Iridochloride Iriduum sesquichloride) IrCl₂ Olive gi sen solid, unsol in acids or alkalıs (Claus, A 107, 129) Obtained by heating Ir black in Cl, also by strongly heating an alkalı double salt of IrCl₂ with cone H₂SO₄ and pouring into cold water (Berzelius, P 18, 470) A soluble hydrate IrCl₃ 4H₂O is obtained by dissolving IrO₄H₄ in HClAq, reducing by H₂S, and evaporating

Double salts Ammonism indium trachloride (Ammonium chloridite) 2(IrCl, 3NH,Cl) 3H,O, formed by slowly evaporating mixed solutions of IrCl, 3NaCl and NH,Cl, or by reducing IrCl, 2NH,ClAq by H,S, adding cone NH,ClAq, filtering if necessary, and slowly evaporating (Claus, J pr 42, 351; Seubert, B. 11, 1761), alive green, rhombe, plates

Potassium chloreridits IrCl, 3KCl 3H2O By reducing IrCl, 2KClAq by H.S, and evaporating with addition of KCl Olive-grien efflorescent prisms The following double salts are also known —2IrCl, (12NH, Co)Cl., IrCl, 3HgCl, IrCl, 3AgCl, IrCl, ENaCl 12H₂O (Claus, lc, Karmrodt a Uhrlaub, A 81, 120)

Iridium TETRACHLORIDE (Iridichloride) The solution obtained by decomposing IrCl, 2NH, Cl suspended in water by Cl contains IrCl. (Vauquelin, A Ch 89, 150, 225), a solution of IrCl, is also obtained by dissolving IrO,H, in HClAq, digesting IrCl, Aq with aqua regia, or decomposing IrCl, 2KCl with H,SiF, Aq (Ber.e hus, P 13, 470) By evaporating these solutions to dryness at temperatures not above 40°, IrCl, is obtained as a black mass, tr nslucent with darkred colour at the edges, very deliquescent, decomposed by heat to IrCl, and Cl, and then to Ir, combines with alkali chlorides to form double salts Ammonium iridium tetrachloride (Ammonium chloriridate) IrCl, 2NH, Cl, obtained by mixing conc solu-tions of NH, Cl and IrCl, or IrCl, 2NaCl Crys tallises from hot water in dark red brown octa hedra, isomorphous with PtCl, 2NH,Cl S 5 in cold water Reduced by SO, to the more soluble IrCl. 3NH,Cl.

Potassium chloriridate IrCl, 2kCl Formed by mixing conc solutions of its constituent salts, also by dissolving IrO,H, in HCl. q (solution probably contains H,IrCl, and adding KCl, also by passing Cl at a gentle heat over an intimate mixture of Ir black and KCl, dissolving in hot water, filtering from Ir, evaporating to dryness with addition of aqua regia, dissolving out KCl by small quantities of cold water, dissolving in hot water, adding a little aqua regia, and evapo rating to the crystallising point Black octa hedra, very sl sol cold water, much more sol hot water, insol alcohol Heated, goes to hot water, insol alcohol Heated, goes to IrCl, 3kCl and at higher temperature to Ir

and KCl

The following chloriridates have also been obtained -IrCl, 2(NH, CH, Cl) (Vincent, C R 100, 112), Ircl, 2NaCl 6H,O (Vauquelin, lc, Berzelius, lc)

Iridium, cyanides of, also Iridicyanides, v

vol n p 332

Iridium, haloid compounds of The only haloid compound certainly formed by direct union of the elements is IrCl, When an intimate mixture of Ir black and KCl is heated in Cl, or of Ir black and KI is heated in I, the double salt K2IrCle or K2IrIe is obtained. The following formulæ present the composition of the haloic compounds and the double salts which they form with alkali haloid compounds - probably with formation of studies, IrO, 2H,O

double alkalı-ırıdıum haloid salts are probably better regarded as salts of the acids H₂IrX₄, H₂IrX₅ and H₂IrX₆ The chlorizidates (salts of H₂IrX₆ and H₂IrX₆ The chloriridates (salts of H₂IrCl₆) are readily reduced to chloriridates (salts of HaIrCla)

Iridium, hydroxides of, v Iridium, oxides and hydrated oxides of

Iridium, iodides of (Oppler, Ueber Iodver bindungen des Iridiums [Göttingen, 1857], J 1857 263) Two iodides, IrI, and IrI, have been isolated There are indications of the existence of IrI, Ir and I do not directly com

IRIDIUM DI IODIDE (Iridoso iodide) brown solid obtained by leading SO, into IrI, suspended in water is perhaps IrI. When a solution of IrCl, 2NH, Cl in boiling KIAq is allowed to cool, a black crystalline powder separates, this is ammonium iridium di iodide, Irl, 2NH,I

IRIDIUM TRI IODIDE (Irido vodide sesqui iodide) IrI, A black crystalline pp , by adding NH Cl to IrI, 2kIAq cold water, more sol hot water Very slightly sol

Double salts - Ammonium iridium tri vodide (Ammonium vodiridite) 2(IrI, 3NH,I) H2O Crystalline needles, by dissolving IrCl, 2NH,Cl in boiling KIAq, cooling, filtering Irl, 2NH, I, concentrating, and recrystallising from hot water

Potassium iodiridite, Irl, 3KI Green lus trous crystalline powder, by reducing IrCl, by H.S with addition of KIAq Silver codiridite, AgI 3KI, has also been obtained

IRIDIUM TETRA IODIDE (Iridi todide) IrCl, black powder, by boiling IrCl, Aq with KI in presence of a little HCl

Double salts -- Ammonium iridium tetra vodide (Ammonium vodiridate) IrI, 2NH,I Se parates after some weeks from solution of IrCl, 2NH,Cl in cold conc KIAq, dark brown lustrous crystals, easily decomposed by heat, aqueous solution gently heated deposits Irl, and IrI, 2NH, I Potassium iodiridate, K, IrI, Sepa rates, after IrI,, from solution of IrCl, in KIAq Also formed by dissolving IrI, in KIAq, and allowing to crystallise, also, in small quantity, by action of I vapour on an intimate mixture of Ir black and kI at 60°-70° Sodium vodiridate, Irl, 2NaI, has also been obtained

Iridium, oxides and hydrated oxides of The only oxides of Ir which have been cer tainly isolated are Ir₂O₂ and IrO The former forms a hydrate with 3H₂O, and another hydrate probably with 5H,O IrO, forms the hydrate ÎrO, 2H,O Hydrated Ir,O, dissolves in alkalis

Double salts. IrX, 3MX IrX, 2MX IrX, IrX₂2MX Br, Br. ? Br, in solution Cl.

None of the Ir haloid compounds has been | dissolves in some acids, but no salts have thus gasified The formulæ are given from the anaother Pt metals The only binary compounds of Pt metals which have been gasified are OsO, and RuO, The and H,IrBr, has been obtained The decomposes again at c 1000°. IrO, is the most Vol. III logies between these compounds and those of

be n prepared Alkaline widates appear to exist. There are indications of the existence of an oxide stable oxide, Ir₂O₈ xH₂O rapidly absorbs O from

the air, and passes into IrO2.xH2O

IRDOUS OXIDE (Iridium monoxide) IrO When IrOl, is boiled with KOHAq a black powder separates, this is probably IrO (Berzelius, P 13, 479) Claus (4 59, 249) thinks that this oxide is obtained by heating one of the double salts of IrSO₂ with K₂CO₃ in a stream of CO₂. On adding KOlAq to IrCl₂ 3NaClAq, and filtering, a solution of IrCl₂ is obtained, when K₂CO₄Aq is added to this liquid (or to IrCl₂ 3KClAq) a greyish green pp is formed, which is probably a hydrate of IrO, the pp is sol in excess of K₂CO₂Aq (Berzelius, Ic) A few salts derived from IrO are known, eg IrSO₂4H₂O, they are not, however, formed directly from the oxide, but by reducing IrO₂2H₂O or chloridates by SO₂

IRIDIC OXIDE AND HYDRATE (Iridium dioxide) IrO, and IrO, 2H,O By adding excess of alkali to IrCl,Aq and heating, a heavy indigo blue pp IrO, 2H,O is produced The same compound is obtained by using IrCl, Aq in place of IrCl, and allowing the pp to stand in the air, when ıt absorbs O The pp is soluble in HClAq with formation of IrCl,, it is insoluble in dilute H₂SO₄Aq or HNO₂Aq When the hydrate is heated in a stream of CO₂, IrO₂ remains as a black powder quite insoluble in acids (Claus, A 59.249) No salts corresponding with IrO2 have been prepared By adding CaOAq to a solution of IrO,H, in HClAq a blue pp is obtained, which is a compound of IrO, with CaO When Ir black is fused for some time with KNO, and the blackish-green mass is treated with water, part dissolves, forming a deep indigo blue solution, and part remains as a black crystalline powder The quantity of K in this powder is variable, but the ratio of Ir O is always 13 (Claus, A 59, 249) The powder is probably an iridate of K, IrO, xK,O

IRIDO-IRIDIC OXIDE AND HYDRATES (Iridium sesquioxide) Ir₂O, and Ir₂O, xH₂O The oxide Ir.O. is obtained by heating IrCl, 2KCl with 2 parts K₂CO₂, or Na₂CO₃, in a stream of CO₂, washing the fused mass with boiling water, and then with water containing NH,Cl, heating to remove NH₄Cl, treating with acid to remove alkali, and again washing with water (Claus, A 59, 249) A hard blue black powder, decomposed by heating to c 1000° into Ir and O (Deville a. Debray, C R 1878 441, cf Disso ciation, vol in p 397) Reduced to Ir by H at the ordinary temperature The hydrate $Ir_2O_2 8H_2O(=IrO_3H_3)$ is obtained by adding to IrCl, 2NaClAq so much KOHAq that all remains dissolved, and then heating or ppg by alcohol Black pp insol in acids except conc HClAq, which dissolves it very slightly By adding a little KOHAq to solution of an alkaline chloriridate, and quite filling a flask with the liquid, a yellow green pp forms, which is probably $Ir_2O_3 5H_2O$, it oxidises very easily to the blue IrO.2H.O, easily soluble in the slightest excess of alkali De Boisbaudran (C R 96, 1236, 1400, 1551) describes a violet coloured pp, which is probably Ir,O, xH,O, obtained by adding alkali to Ir,(SO,), 3K,SO,Aq (this salt is formed by heating Ir compounds with KHSO, and treating the product with K2SO,Aq) salts, and some double and basic salts, corresponding with Ir.O. are known, they are pro-

duced indirectly. The sulphites and double sulphites are produced by reducing IrO₂2H₂O or information by SO₂. By adding CaOAq to IrCl₂Aq a yellow pp of Ir₂O₃ 3CaO is produced (Claus, 4 59, 249). Compounds of Ir₂O₃ with NO₂ and with intries are described by Gibbs (B 4, 280).

Iridium, oxychloride of An oxychloride of Ir is said by Berzelius (P 18, 484) to be formed as a yellowish-brown pp by adding a small quantity of HgNO₂Aq to IrCl₄2KClAq, HgCl₃ goes into solution, addition of more HgNO₃

causes ppn of HgCl

Iridium, phosphide of. When Ir is very strongly heated with 1 its weight of P, the whole melts By heating the product with CaO the P is removed Ir and P probably combine when heated together, but no phosphile of Ir has been isolated

Iridium, salts of Very few salts of 1r are known other than the haloid compounds Iridous sulphite, IrSO, 4H₂O, and some double sulphites, irido iridio sulphite, Ir₂(SO₂), 6H₂O, and several double and basic sulphites, and a few other salts (chiefly double and basic), corresponding with Ir₂O₂, have been isolated None of these salts is obtained from the corresponding oxide, the sulphites, which are the best known salts, are formed by reducing IrO₂.2H O, or chloriridates, by SO₂Aq

Iridium, sulphides of Three sulphides of Ir are known, IrS, Ir.S₁, and IrS₂ Ir combines

with S when heated with it

IRIDOUS SULPHIDF IRS (Iridium monosul phide) A blue black solid, by heating Ir S₂ or IrS₂ (Berzelius, P 13, 487, Böttger, J pr 8, 227) The pp obtained by passing H₂S into a solution of an iridous compound is probably IrS Does not decompose by heating in absence of air, roasted in air gives SO₂ and a basic sulphate The ppd sulphide dissolves in KHSAq

IRIDIC SULFHIDE IrS₂ (Iridium disulphide) A black powder, obtained by strongly heating Ir black with S and Na₂CO₃, and washing with water (Fellenberg, P 50, 66) Heated in air gives SO₂ and Ir Berzelius (lc) obtained a dark brownish-yellow pp by passing H₂S into IrCl₃Aq, heated, this gave IrS

IRIDO IRIDIO SULPHIDE Ir₂S. (Iridium sesqui sulphide) A brown black pp by passing H₂S into solution of an irido iridic compound Heated gives SO₂ and S, and leaves IrS (Berrelius, Ic)

M M P M

IRIDOLINE $C_{10}H_9N$ (252°-257°, S G 15 1072 A base occurring in coal tar oil (G Williams, Tr E 21, 377, C J 16, 375)

IRIDOSMIUM v Iridium, Alloys of, p 47
IRIS CAMPHOR C₈H₁₆O₂ Occurs in the root of Iris florentina (Dunas, A 15, 158) Pearly plates, volatile with steam Insol water Fluckiger (Ar Ph [3] 8, 481), by distilling iris root with steam, obtained crystals of myristic acid saturated with a fragrant oil

IRISH PEARL MOSS v Caragneen moss IRISIN $6C_aH_{10}O_s$ ag $[a]_D=-51^\circ$ A carbohydrate extracted from the rhizomes of the water lily (*Iris pseud acorus*) with water and then ppd with lead acetate Probably identical with graminin (Wallach, A 284, 384, B 21, 396)

Properties — More strongly laworotatory than inulin —1 Does not reduce Fehling's solu-

IRON. 51

tion Is very easily converted into sugar (chiefly levulose) by weak acids. Gives no colouration with iodine V sol strong HI solution from which solution NaOH separates iodoform. Also sol HCl, and NaOH. Irisin is nearly 4 times as soluble as inulin in water at 22°. Under the microscope the globules of irisin resemble those of inulin, but do not exhibit double refraction.

IRON Fe At w 559 Mol weight un known [1550°] (Poullet), [1587°] (Daniel), Tr 1880), [1600°] (Pictet, P M 1879 446) SG determinations vary from 6 95 (Roberts a Wrightson, A Ch [5] 30, 274) to c 82 Almost pure Fe has SG c 7 85 *t 16° according to Caron (C R 70, 1263), 8 139 according to Chandler-Roberts (C N 31, 137) SH 111641 at 0°, 112359 at50°, 118795 at 10° (Byström, Oefvers k Vetensk Forrhandl [Stockholm, 1860] 17, 307, v also Weinhold, P 149, 214) CE 0000, 233 at 13° to 100° (Kopp, A 81, 1, v also Fizeau, A Ch [4] 2, 143, C R 68, 1125) T C (Ag = 100) 11 9 (Wiedemann a Franz, P 89, 497) E C (Hg at 0° = 1) 9 68 at 0°, 6 19 at 100° (Lorenz W 13, 422, 582) Crystallises in regular system (Fuchs, A 84, 257) Emission spectrum is very complex (Angström, P 94, 141, Cornu, Spectre Normal [Paris, 1881], Liveing a Dewar, Pr 29, 402, 32, 402) Some of the thermal data for Fe are presented in the following table (Th 3, 293) —

 $X [Fe, X^2, Aq]$ Cl = 99,950 Br = 78,070 I = 47,650

 $\begin{array}{c} I = 47,650 \\ [\text{Fe,Cl}^{\bullet},\text{Aq}] = 127,720 \; , \; [\text{Fe',O'},3\text{H}^{2}\text{O}] = 191,150 \; , \\ [\text{Fe}^{2}\text{O'},\text{H}^{\bullet},3\text{H} \; \text{SO'},\text{Aq}] = 33,840 \; , \\ [\text{Fe,H'},\text{SO'},\text{Aq}] = 24,840 \end{array}$

For further details regarding physical properties v Rammelsberg's Hand der hyst physikal Chemie, 1, 193 For the physical properties of different kinds of pig iron, wrought iron, and steel, v Diotionary of Applied Chemistry

Occurrence — The metal itself is found in small quantities in rocks of volcanic origin and in lavas, it also occurs in meteorites. Compounds of iron are very widely distributed, and occur in immense quantities. The spectroscope shows the existence of iron (or iron compounds) in the sun and other stars. The chief ores of iron are hamatite, FeO, brown iron ore, FeO, H₂O, yellow ochie, FeO, 2H₂O, magnetic iron ore, FeO, spathic ore, FeCO, pyrites, FeS, (the 'ormulæ express approximately the compositions of the ores)

Preparation —Commercial iron, whether pig iron, malleable iron, or steel, always contains more or less C and Si, and generally small quantities of P and S, sometimes also traces of Mn, Ti, Ni, Co, Cu, Sb, and As 1 Wöhler (A 94, 125, 95, 192) prepares Fe₂O₅ by heating FeSO₄ crystals with 2-3 parts NaCl in a crucible and washing with water, and reduces the Fe₂O₅ by heating in H (cf G de Claubry, C C 1859 214, Luca, C R 1851 332, 1852, 202). Moissan (C R 89, 176) says the reduction must be carried out at c 700°—2 By reducing FeCl₂ in a stream of H (Peligot, C R 19, 670), or in neutral solution at b point by Zn (Capitaine, C R 9, 757), or by Zn vapour at a high temperature (Poumarèds, C R 29, 518)—3 Troost melts

pig iron in a lime crucible by the O-H flame (BL [2]9,250)—4 A mixture of dry Na,80, and FeSO, is heated in a Pt crucible so long as SO, comes off, the residue is washed with cold water, and the crystalline Fe,O, is reduced in H in a Pt crucible, and the Fe is melted in the O-H flame (Ma'thiessen a Prus Szczepanowski, C N 20, 501)—5 By electrolysing FeSO,4q saturated with NH,Cl, Fe appears at the negative pole (a large iron plate), it contains H and other gases, which may be removed by heating (Varrentrap, D P J 187, 152, Lenz, J pr 108, 438)

D P J 187, 152, Lenz, J pr 108, 438)
Properties —A lustrous, greyish white metal Crystallises in regular cubes or octahedra Annealed wrought iron wire is extremely tenacious. Such mechanical treatment as hammering, bending, or torsion changes many of the physical The physical properties properties of iron which have been determined are for the most part those of iron containing small quantities of foreign substances Iron is magnetic (cf Faraday, P 70, 24, Gore, P M [4] 40, 170) Pure, or almost pure, Fe is softer and more malleable, but less tenacious, than ordinary malleable iron The iron obtained by reducing Fe₂O₂ in H at temperatures below c 600° is pyrophoric, the powder obtained at c 700° is non pyrophoric (Moissan, C R 89, 176) By passing a weak electric current through FeSO₂Aq mixed with MgSO, Lenz (C C 1870 188) obtained a greyish, non crystalline, very brittle mass, easily pulverised by the finger, this iron contained c 200 times its volume of gases, chiefly H (v Iron, hydrides of), mixed with CO, CO2, N, and H2O vapour, by heating in vacuo the gases were removed, and the iron then resembled Pt in appearance Iron is unchanged in dry O, but in moist O or in ordinary air it is slowly oxidised to $\Gamma \in O_1 \times H_2O_1$, heated in air or O a mixture of Fe O, and Fe,O, is produced Iron combines directly with the halogens, also with S, C, B, Si, P, As, it forms alloys with many metals Iron dissolves in the common mineral acids with formation of salts Finely divided Fe decomposes water at 100°

The atomic weight of Fe has been determined (1) by analysing and determining V.D of FeCl₂ and FeCl₂, (2) by determining S H of Fe, (3) by reducing Fe,O₂ in H (Berzelius, P 8, 165, Svanberg a Norlin, A 50, 432, Erdmann a Marchand, J pr 33, 5, Rivot, A Ch [3] 30, 192), (4) by transforming Fe into Fe,O₃ (B, A 50, 432, S a N, lc, Maumené, A Ch [3] 30, 380), (5) by determining the Cl in FeCl₂ and in FeCl₃ (Dumas, A Ch [3] 55, 157) The atom of Fe is trivalent in the gaseous molecule FeCl₃, and divalent in the gaseous molecule FeCl₂ (v Iron, chlorudes of)

Iron is distinctly a metallic element, it replaces the H of most acids, forming two series of salts, the simplest formulæ for which are FeX_2 and FeX_3 respectively, X = Cl, NO_2 , SO_4 , PO_4 &c The ferrous salts, FeX_2 , are

 $\frac{SO_4}{2}$, $\frac{FO_4}{8}$ do The ferrous salts, FeX₂, are easily oxidised to ferric salts, FeX₂, very many salts, both normal and basic, of both series have been isolated, numerous double salts

have been isolated, numerous double salts are also known. Fe₂O₂ forms compounds with several oxides more basic than itself, eg with K₂O, BaO, CaO, MgO, these compounds may be

52 IRON

regarded as ferrites derived from the hydroxide $\mathbf{Fe}_2\mathbf{O}_4\mathbf{H}_2(=\mathbf{Fe}_2\mathbf{O}_3\mathbf{H}_2\mathbf{O})$ There are also some salts known as ferrates, e g K₂FeO₄ and BaFeO₄, which may be looked on as derived from the hypothetical ferric acid H2FeO4, but neither this acid nor its anhydride, FeO₃, has been isolated (v FERRATES and FERRITES, vol 11 pp 546-7) Fe₂S₃, like Fe₂O₄, forms some double compounds with more basic sulphides, these double compounds may be regarded as thioferrites (v Iron, sulphides of) Fe is closely related to Co and Ni, these three metals show some marked analogies with the Pt metals, Fe is also related to Cr and Mn, and it shows some resemblance to Al and the other earth metals (v Iron Group OF ELEMENTS, also Noble METALS, and cf CHROMIUM GROUP OF ELEMENTS, and EARTHS, METALS OF THE)

Reactions and Combinations -1 Heated in aw or oxygen Fe is oxidised to Fe₂O₃ and Fe₃O₄ 2 Unchanged in dry air at ordinary temperature, but rusts in moist air to Fe₂O₃ xH₂O -Finely divided Fe decomposes water at 100° (v Ramann, B 14, 1433), and rapidly decom poses steam Compact Fe decomposes steam at red-heat, Fe₃O, 18 produced Iron slowly rusts in contact with water and ordinary air, the formation of Fe₂O₃ xH₂O proceeds slowly at first, and then more rapidly, probably because the Fe and Fe₂O₂ exert an electrolytic action on the water, presence of ammoniacal salts increases the rate of rusting, alkalis and alkaline carbonates hinder the rusting According to Calvert (C N 23, 98) Fe does not rust in water if CO₂ is absent For an account of the retard ing or hastening action of various salts on the rusting of Fe v Wagner, D P J 218, 70 Various processes have been used for preventing iron rusting, covering the iron with Zn is frequently done, Barff a Bower heat the iron to c 650° in water vapour, whereby a hard protect ing film of Fe,O4 is formed on the surface of the iron —4 Fe decomposes solution of hydrogen peroxide, forming Fe₂O₅H₆, the Fe becomes covered with bubbles of O (Weltzien, A 138, 129) -5 Iron dissolves in dilute sulphuric or hydrochloric acid with evolution of H conc sulphuric acid is almost without action on Fe, when heated, SO₂ is evolved, and Fe₂(SO₄)₂ formed Dilute nitric acid dissolves Fe, forming Fe(NO₃)₂ and NH₄NO₃ with evolution of N oxides Conc nitric acid is almost without action on Fe, v infra, Passivity of iron -6 Heated repeatedly with caustic soda solution Fe forms crystals of Fe₂O₃ H₂O (Brunck a Graebe, B 13, 725) -7 When Fe is heated to redness in a stream of ammonia a nitride of Fe is formed, Fe, N, according to Stahlschmidt (P 125, 37) — 8 Fe heated in a closed tube with solution of sulphur dioxide to 200° forms solution of FeSO, and FeS₂O₂, and crystals of FeS₂ (Gentner, A 129, 350) —9 Fe is oxidised to Fe₂O₂, or K₂FeO₄ (v vol. 11 p 547) by fusion with potassium nutrate -10 Fe combines with the halogens, with arsenic, boron, carbon, hydrogen, nitrogen, phosphorus, and sulphur (v Iron, chlorides of, borides of, corbides of, &c), it also folms alloys with several metals (v Iron, alloys of)

Passesty of eron Iron is not acted on by cone nitric acid, iron which has been immersed in cone nitric acid does not dissolve in dilute

nitric soid, nor does t ppt Cu from CuSO, Aq; such Fe is said to be passive Co and Ni, and per laps B1, also show passivity According to Varenne (A Ch [5] 19, 251, 20, 240) immersion of iron in soid of 100 pc HNO, is not accompanied by evolution of any gas, if the acid has SG 1382 (c 63 pc HNO₃) NO is evolved coprously for 3 to 20 records and then ceases. in. both cases the Fe becomes passive Acid of less SG than 1 299 (c 47 nc HNO_s) does not pro duce passivity If part of a rod of Fe is dipped into conc acid, and then the whole is carefully immersed in a dilute acid, the whole rod is pas-These facts are e-plained by Varenne by supposing that a gaseous film is deposited on the surface of the iron, and protects the iron from the action of the ac 1, the gas dissolves in the more dilute acid, in the case of the partly immersed rod the gas bubbles are removed from one part and then adhere to the other part of the rod This view was also upheld by Mousson (P 39, 330), but was controverted by Faraday and Schönbein (P 39,342), and Beetz (P 67,286,365) Ramann (B 14,1430) considers the passivity to be due to a layer of Fe,O,, which is soluble in dilute, but insoluble in cone , nitric acid R thinks that immersion in the acid produces Fe(NO₃), and that this then reacts with the Fe to produce Fe₃O, and NH,NO₃, iron wire, according to R, becomes passive when partly heated, also by making it the positive electrode in an O containing liquid Various oxidising agents acting on Fe render it passive, eg HClO₃, CrO₃, H₂O₂ (Keir) The passivity of Fe 13 removed by strongly rubbing the iron, or heating it in reducing gases, also by bringing it into contact According to Saint Edme (C R 106, 1079) commercial sheet Ni is passive in ordinary HNO, Aq, Fe in contact with Ni becomes passive in the acid, passive Ni remains passive when heated to bright redness in H, whereas Fe loses its passivity

Detection and Estimation —Fe compounds are detected by giving a reddish green colour to the hot borax bead in the oxidising flame, which becomes bottle green to nearly colourless when cold, also by the ppn, of brown red Fe₂O₃xH₂O by alkalis from ferric compounds, K₃FeCy₆Aq gives a deep blue pp with ferrous salts, and no pp but a brownish colour with ferric salts Fe is estimated, gravimetrically, by ppn as Fe₂O₃xH₂O and weighing as Fe₂O₃, volumetrically, by titration with KMnO₄Aq or K₂Cr₂O₃Aq For details and for other methods v lanuals of Analysis

Metallurgy of von Pure iron is too soft and has too little tenacty for use in making machinery, &c Ordinary iron is divided into three kinds pig or cast iron containing from 2 to 5 75 pc C, bosides small quantities of Si, P, S, and traces of metals other than Fe (chiefly As, Ti, V, Cr, Mn, Cu), malleable or wrought iron containing less than 5 pc C, and steel containing about 1 pc C Pig iron is obtained by very strongly heating Fe ores with lime and coal in large furnaces, and blowing in air at the bottom of the furnaces, the C of the coal is burnt chiefly to CO, and this reacting with oxides of Fe produces Fe, which then combines with, or it may be only dissolves, carbon, the C seems to be produced by a reaction between the partly reduced Fe,O.

and CO (v Bell, C J [2] 7, 203) The reduction of Fe₂O₃ is probably sided by cyanides present in The greater part of the for agn the furnace matter of the iron ores is removed in the form of a fusible slag consisting of silicate of Fe, Ca, Mg, Al, Mn, &c Wlought iron is obtained by puddling cast iron, in this process the cast iron is strongly heated along with lumps of Fe.O. in a reverberatory furnace, the Fe₂O, is partially deoxidised, and the O is used in burning the C, Si, S, and P, the C being thus almost entirely removed as CO or CO, Steel is obtained by com pletely removing the C from wrought iron by blowing in air, and then adding a sufficient quan tity of Fe containing a known quantity of C Steel is also rometimes made by causing wrought aron to take up C by stro gly heating the iron with charcoal Cast iron is more fusible, harder, and more brittle than wrought iron, which is more ductile and malleable than cast iron Steel combines the malleability and ductility of wrought iron with the fusibility of cast iron, at is also very hard and elastic Cast iron is divided into two kinds grey cast iron, granular, with low malleability, SG c 71, melting at c 1600°, this variety contains C partly in combination with Fe and partly un combined as graphite, white cast iron, harder but not so strong as grey, SG c 75, melts at a lower temperature than grey, this variety contains only combined C By me ing grey, and cooling rapidly, white, cast iron is obtained, by melting white, and cooling slowly, grey, cast iron as produced I or details of the metallurgy of iron v Dictionary of Apilifd Chemistry

Iron, alloys of Iron alloys with many me tals, the softer metals—Ag, Sn, Zn &c—become harder and more tenacious when alloyed with a few parts of iron per thousand, the alloys may generally be prepared by fusing the various metals with iron wire, a little I e₂O₂ being added

to remove C from the iron

Alloys with aluminium have been described, approximately Al.Fe (Wohler, A 115, 102) ap proximately Al.Fe, and All'e, (Calvert a John son, J 185a 32b) Sonnenschein (J pr 66, 168) described an alloy with lead having a com position approximating to Ph.Fe An amalgam of iron is formed by mixing finely divided he with Na amalgam, adding a little water, and squeez ing out excess of Hg, the crystals correspond in composition to Hg, Fe, , they slowly undergo de composition, rapidly when much compressed (Raman., B 14, 1433) Alloys with the fol lowing metals have been described --Sb, Cu (Musket, P M [3] 6, 81), Mn (M, lc), Mo (Heine, J pr 9, 176, Stromeyer, P 28, 551, Wiggens, P 28, 565, Steinberg, J pr 18, 379), Ni, Pd (Faraday a Stodart, Tr 1822 254), Pt (Schönbein, P 42, 17, Boussingault, A Ch [2] 53, 441), K (Calvert, P M 1855), Rh (F a S, &c), Sn (Lassingne, J Chim med 6, 609), Ti (Riley, C J 16, 387), W (Bernouilli, P 21, 573), Zn (Percy, Metallurgy, 2, 153)
Iron, arsenides of The minerals arsenical

Iron, arsenides of The minerals arsenical pyrites and mispickel are compounds of Fe with As and with As and S respectively, their compositions approximate to the formulæ FeAs, and FeAsS Brittle masses are obtained by fusing together As and Fe out of contact with air, but

they have not been much examined

Iron, borides of When Fe is heated in a stream of BCl, vapour, a hard, white substance is obtained, which is decomposed by boiling water forming H₂BO₂ (? and Fe₂O₃), and evolving H (Fremy, Wurtz's Dict de clim 1, 1417) by heating ferric borate in H, Lassaigne (J Chim met 3, 535) obtained a similar compound, no analyses are given

Iron, bromides of Two exist, FeBr, and FeBr,, both are produced by the direct union of their elements. Neither has been gasified, the formula are given because of the analogues between these salts and FeCl, and FeCl, (v Iron,

chlorides of)

FERROUS BROMIDE (Protobromide of 1ron)
FeBr₂ A yellow solid, obtained by heating
excess of Fe in Br vapour, soluble in water,
solution deposits crystals FeBr₂ 6H₂O, decom
posed by heating in air to FeBr₃ and Fe₂O₃
(Scheufelen, A 231, 156) Thomsen gives
[Fe,Br²,Aq] = 78,070 (Th 3, 294)

Ferric Bromide (Sesquibronide of iron)
FeBr, Dark red crystals, obtained by heating
Fe in excess of Br vapour, may be sublimed,
with partial decomposition, out of contact with
air, deliquescent Aqueous solution very easily
partially reduced by heating to FeBr, (L de
koninck, Zeit anorgan Chemi, 1889 149)

Iron, carbides of Whether pig iron is a carbide of iron, or a mixture of carbides and free C, cannot yet be regarded as finally settled The presence of a few per cents of C in iron very much modifies the properties of the whole, by making it more fusible, if from 2 to 15 p C is piesent, the mass is only fusible with difficulty, but is very hard and tough, it has the properties of wrought iron or steel, according to the quantity of C Iron takes up C directly, and by so doing has its properties changed On the temperatures at which carburation of Fe occurs with amorphous C, diamond, and graphite, t Hempel, B 18, 998

The following carbides of Fe have been described, but the investigation of none of these bodies is complete —(1) Fe₁C, a brittle, fusible mass, by melting together an intimate mixture of equal parts of Fe and C (Faraday a Stodart, G A 66, 183), (2) FeC₂, a black pyrophonic powder, by heating H₄FeCy₅, or (NH₄)₄FeCy₅, out of contact with air (Berzelius), or by fusing K₄FeCy₅, and washing away the KCN produced (Rammelsberg), (3) FeC₅, was obtained by Karsten by the action of dilute acids on grey pig-iron (S 68, 182), (4) FeC, by the action of Br or I on pig iron (Berthier, J 1862 127)

Iron, chlorides of Two chlorides of iron, FeCl, and FeCl, have been isolated, and a third, Fe,Cl, perhaps exists When Fe is heated in a stream of Cl, both FeCl, and FeCl, are pro-

duced

Ferrous chloride FeCl₂ (Iron dichloride on protochloride) Mol w 126 64 (v infra) S G 2 528 (Filhol, A Ch [3] 21, 415), 2 988 at 17 9° (Clarke's Specific Gravity Tables [new ed] 24) V D 62 79 at 1300°-1400°, 61 55 at 1400°, 1500° (Nilson a Pettersson, C J 53, 828) V D at Jellow heat 94 4 (V Meyer, B 17, 1335), calc for FeCl₂ 63 32, for Fe₂Cl₃ 26 64 (v infra). H.F [Fe,Cl²] = 82,050, [Fe,Cl²,Aq] = 99,950; [FeCl²,4H²O] = 15,150 (Th 3,293)

Formation.—1. By heating excess of Fe filings

or wire in Cl.—2 By partially reducing FeCl, in H (Wöhler, A 4, 255) -3 By dissolving Fe in HClAq out of contact with air, evaporating, and drying in a stream of H—4 By heating Fe filings with NH Cl out of contact with air

Preparation — Fe wire is heated in a stream of dry HCl, and the product sublimed in the same

gas (Wöhler a Liebig, P 21, 258)

Properties and Reactions - White, lustrous, six-sided, deliquescent, tablets Heated very strongly in N forms FeCl, and Fe (V Meyer, B Heated in O, forms Fe,O, with evo-17, 1335) lution of Cl Oxidises readily in air to a mixture of FeCl, and Fe₂O₃. Heated to redness in steam forms Fe₃O₄, HCl, and H. Heated to red ness in a stream of NH, Fe, N, is produced (Fremy, C R 52, 321) Heated with PH, forms HCl and Fe phosphide A mixture of FeCl, and O is reduced by Zn vapour with separation of Fe ın crystals (Poumarède, C R 29, 520) S c 50 at 80°, less sol in HClAq

Molecular weight of gaseous ferrous chloride By volatilising in HCl at a yellow heat, V Meyer got values for V D which were about the mean between those calculated for FeCl, and Fe_2Cl_4 (B 17, 1335), calculated for $FeCl_2 = 6332$, for $Fe_1Cl_4 = 126.64$, observed 92.32 and 96.51 Meyer concluded that molecules of Fe,Cl, pro bably exist at lower temperatures and molecules of FeCl₂ at a very high temperature Nilson a Pettersson (C J 53, 827) obtained values for V.D at c 1400° agreeing with that calculated for FeCl₂, calculated = 6332, observed at 1300° $1400^{\circ} = 6279$, at $1400^{\circ} - 1500^{\circ} = 6155$ can be no doubt then that molecules of the com position FeCl₂ exist at c 1300°-1500°

Combinations -1 With water to form the hydrates FeCl, 2H2O and FeCl, 4H2O The for mer is obtained by saturating warm conc HClAq with FeCl₂ or by passing HCl into saturated FeCl, Aq, the latter is produced by dissolving Fe in HClAq and concentrating out of contact with air FeCl₂ 4H₂O forms blue green, monoclinic, deliquescent, transparent crystals, SG 193—2 With nitric oxide, solution of FeCl₂, especially an alkaline solution, absorbs NO forming a green-brown liquid which contains FeCl, NO, NO is removed by warming -3 With ammonia to form FeCl₂ 6NH, and 3FeCl₂ 2NH, (Rog stadius, J pr 86, 310) The former is a white powder, produced by passing NH, over FeCl, at the ordinary temperature, the latter is formed by slowly heating FeCl, 6NH, to melting strongly heating 3FeCl., 2NH, in NH, the nitride Fe, N, 1s formed (Fremy, C R 52, 321) -4 With ammonium chloride to form FeCl, 2NH, Cl, obtained by crystallising mixed solutions of FeCl, and NH,Cl, or, according to Hisinger a Berzelius (G A 27, 273) (with evolution of NH, and H), by boiling Fe filings with NH,ClAq (cf. Winkler, R. P. 59, 171, Vogel, J pr 2, 192) A compound FeCl₂2KCl 2H₂O is also known (Scha bus, W A B 1850 475) Compounds with CdCl, and HgCl, viz FeCl, 2CdCl, 12H,O and FeCl, HgCl, 4H,O are also described (v Hauer, W. A B 17, 331)

FERRIC CHLORIDE (Iron sesquichloride o perchloride) FeCl. Mol w 162 01, and probably also 324 02 (v mfra) (280°-285°) (Friedel a. Crafts, C. R 107, 801) S G 2804 at 10 8° (Clarke's Tables of Specific Gravity [new ed.], FeCl, is soluble in alcohol or ether, the solution

24) VD varies from c 165 at 320° to c 80 at 1000°-1800° (v infra) Crystallises in hexagonal forms a c = 1 1 235, Nordenskiöld (v. Rammels berg's Hand der Krystal physikal Chemie, 1, 260) H F [Fe,Cl*] = 96,040, [FeCl*,Cl] = 13,990, [Fe,Cl*,Aq] = 127,720, [FeCl*Aq,Cl] = 27,770 (Th 8, 293)

Occurrence —In the craters of volcanoes
Formation —1 By heating Fe in a stream of Cl -2 By heating FeCt, in Cl -3 By strongly heating FeCl, in a wide mouthed vessel, Fe₂O, remains and FeCl₃ sublimes —4 By passing HCl over strongly heated amorphous Fe₂O₃ (Deville a 1 roost, C R 45, 821) -5 By heating a mix ture of calcined FeSO, with CaCl2 or NaCl The product obtained by boiling dowr a solution of Fe₂O₃ in HCl always contains oxychloride

Preparation - Fine iron wie is strongly heated in a hard glass tube in a stream of dry Cl, and the product is sublimed in the same gas

To prepare a solution of FeCl, hydrated Fe O_3 is dissolved in hot $HCl\Lambda q$, the solution is decanted, Cl is passed in until K.FeCy, ceases to give any trace of blue colour, and excess of Cl is removed by warming, or 2 parts warm EClAq are saturated with Fe (filings or wire), to the clear decanted liquid 1 part HClAq is added, the liquid is warmed and HNO, Aq is added little by little until all FeCl, is oxidised to FeCl, excess of HNO, is removed by evaporation with a little HClAq Geissler (Ar Ph [2] 58, 159) recommends to evaporate the ferrous solution to S G 1 3 at 17° and then to add HNO, Aq to the cold solution, when oxidation proceeds rapidly

Properties -By slowly cooling the vapour, FeCl, condenses in hexagonal crystals which appear very dark red by transmitted, and green ish by reflected, light (Deville a Troost, C h As ordinarily prepared FeCl, forms a 45, 821) brownish black crystalline mass Volatilises at somewhat over 100° Melts at 306°-307° in a sealed tube (Carnelley a Williams, C J 37, 126) Deliquescent, conc solution in water is dark brown and somewhat viscid, it becomes limpid

and yellow on dilution, a very dilute solution is colourless when cold (v. Reactions, No. 4)

Franz (J. pr. [2] 5, 283) gives the following table showing S.G. and percentage composition of FeCl,Aq at 17 5° -

8 G	p c. FeCl.	8.G	p c. FeOl.	8.0	p c FeOl
1 0146	2	1.1746	22	1 3870	42
1 0292	4	1 1950	24	1 4118	44
1 0439	6	1 2155	26	1 4307	46
1 0578	8	1 2865	28	1 4617	48
10734	10	1 2568	30	1 4876	50
1 0894	12	1 2778	32	1 5153	52
1 1054	14	1 2988	34	1 5439	54
1 1215	16	1 3199	36	1 5729	56
1 1378	18	1 3411	38	1 6023	58
1 1542	20	1 8622	40	1 6317	60

Schult (Forh skand Natur, 1868 452) obtained the following results at 14 6° -

G FeCl,Aq		S.G FeCl,Aq	p c. FeCl.
1 0382	4 65	1 339	88 25
1 0918	10 45	1 3824	86 95
1 1517	16 80	1 4361	410
1 2107	22 54	1 554	49 61
1 2818	24 60	il	

easily decomposes in sunlight with formation of FeCl.

Molecular weight of gaseous ferric chloru. 3 Deville a Troost (C R 45, 821) found the V D of ferric chloride at 440° to be 1627, this corresponds to the formula Fe₂Cl₄ Grunewald a V Meyer (B 21, 687) made a series of determinations of V D, in an atmosphere of N, with the following results 151 75 at 448° (mean of 4), 138 5 at 518° (mean or 3), 121 3 at 606° (mean of 6), 78 66 at 750° (mean of 2), 71 2 at 1036°, 77 6 at 1077°, .43 at 1300° These numbers seem to indicate a gradual resolution of mole cules of Fe₁Cl₂ into FoCl₃, none of the results, however, agrees exactly with the value calculated for FeCl, (81 '005), but this was to be expected, as G a M showed that even at 518° ferric chloride is partially resolved into FeCl, and Cl in an atmosphere of N According to Friedel a Crates (C R 107, 301) ferric chloride is not dissociated at 440° in an atmosphere of Cl, F a C made a series of determinations of VD in Cl, using a modification of Dumas' method, the results are appended —165 1 at 321 6°, 180 4 at 325 2°, 174 2 at 356 9°, 171 5 at 357°, 168 7 and 163 5 at 412 23 These values are all somewhat greater than 1621, the value required by the The most probable conclusion formula Fe Cl from all the results seems to be that at high temperatures, c 700° and upwards, the vapour of ferric chloride consists of molecules of FeCl, but that as temperature falls these molecules are mixed with more complex molecules, some of which at any rate have the composition Fe,Cl,

(cf Young, N 39, 195)
Reactions -1 When FeCl, is heated in oxy gen, Fe,O, and Cl are produced (cf Schulze, J pr [2] 21, 407) -2 Heated in hydrogen, FeCl. is formed (Wohler, A Suppl 4, 255) -3 Heated in water vapour, Fe₂O₃ and HCl are formed -4 FeCl, dissolves in uater, the conc solution is a syrupy dark brown liquid, becoming yellow on dilution, and colourless when very dilute and By heating FeCl, Aq, colloidal soluble Fe,O, xHO and HCl are produced, fairly conc FeCl, Aq forms oxychlorides, Fe2O, xFeCl,, at o 100°, and at higher temperatures Fe₂O, is formed The amount of decomposition and the composition of the products depend on the con centration of the solution and the temperature, very dilute solutions, c 30,000 water to 1 FeCl,, are decomposed with formation of colloidal soluble ferric hydrate even without warming (cf Iron, hydrated oxides or hydroxides of, p 59) Krecke (J pr [2] 3, 280) gives the following table (cf Tichborne, C N 24, 123 199, 209, 230, 25, 133, Muller, J 1873 40, Fous sereau, C R 103, 42) —

FeCl, Aq containing \(\frac{1}{16} \) p c FeCl, or less is de composed by light at 5°-6° (Krecke, \(l \, c \)) When FeCl, Aq is heated in a sealed tube to 250°-300° it decomposes to Fe₂O₂ and HCl (Senarmont, C R 32, 762) From a very dilute cold colourless solution of FeCl, K, FeCy, Aq ppts a pure blue pp, and NaCl produces no change If the solution is heated it becomes yellow, and contains soluble ferric hydrate and HCl From this solution K, FeCy, Aq ppts greenish blue solid, and on addition of NaCl a soluble ferric hydrate separates, which, after long contact with NaClAq, becomes insol in water (Debray, C R 68, 913). Evaporation of FeCl.Aq is accompanied by evolution of some HCl, the residue contains oxychloride or hydrated oxide FeCl, is not volati lised from violently boiling FeCl, Aq containing HCl (Fresenius, Fr 6, 92) G Wiedemann con HCl (Fresenius, Fr 6, 92) nects the decomposition of FeCl, Aq, and also of other ferric salts, with the different magnetic behaviour of colloidal soluble Fe₂O₃.xH₂O, and that hydrate which remains in combination with the acid (W 5, 45) -5 FeCl, dissolves in alcohol or An ethereal solution mixed with alcohol and allowed to stand in sunlight loses its yellow colour, and FeCl, and chlorinated derivatives of alcohol and ether are formed.-6 An aqueous solution of FeCl, 18 readily reduced to FeCl, e g by As, Sb, Bi, Fe, Pb, or Zn, also by finely divided Pt, more slowly by Pd and Au (cf Béchamp, C R 52, 757, Saint Pierre, C R 54, 1077). 1077) Also reduced by stannous chloride, sul phurous acid, or sulphuretted hydrogen, hydriodis acid reduces dilute FeCl, Aq slowly (v Mohr, A Many organic compounds also reduce FeCl, Aq, especially in sunlight, eg alcohol and ether, or tartaric acid (v Schoras, B 3, 11, Poitevin, C R 52, 94) -7 A very little FeCl, 18 said to be formed by passing hydrogen for 48 hours through FeCl, Aq (Brunner, J 1864 125) — 8 FeCl, dissolves freshly ppd ferric hydrats forming oxychlorides (q v) — 9 When FeCl, Aq is dropped into solution of potassium nitrite, in an atmosphere of CO, brisk evolution of NO proceeds, and a pp of soluble ferric metahydroxide, Fe₂O₃HO, separates (Pesci, G 18, 183)— 10 FeCl₂Aq reacts with potassium todide to form FeCl₂, I, and KCl, probably FeI₁ is at first produced, and is then resolved into Fel. and I, and then the FeI, reacting with unchanged FeCl, forms FeCl, and I (v Carnegie, C N 60, 87)—11 When electrolysed, conc FeCl, Aq gives FeCl, at the negative, and Cl with a little O at the positive, electrode

Combinations —1 With water to form various hydrates (1) FeCl, 6H O, yellow solid, formed by dissolving 100 parts FeCl, in 63 5 parts H₂O (S G of solution 167 at 25°), or by slowly eva-

P.o. FeCl, in solution		on of Graham's idal hydrate	Formation of colloidal hydrate of P de Saint-Gilles	Formation of oxychlorides	Formation of Fe _s O _s
рс. 82	100-130		•	over 100	1 4 0
16		eCl, re formed	_		120
8	100-110	on cooling		31 31	110
Ă	90-100	· ••••		90	
ž	87			87	
ī	83 \		100-130		
•5	75	eCl, not re forme	. "		
25	04:7	on cocling	. »		
125	54	on cocuing	**		
•0625	36)		•		

ing to crystallise, or by exposing FeCl, to the air (Mohr, A 29, 178), or by passing HCl over commercial ferric chloride, filtering the liquid which forms through glass wool, and evapora ting over KOH in vacuo (Engel, C R 104, 1708), melts at 35 5°, and solidifies again at 28° (Ord-way, Z 1866 23) (2) 2FeCl, 5H₂O, reddish tablets, melting at 31°, formed by melting the hexahydrate, warming to 100°, for some hours, and cooling slowly (Engel, lc), or by evaporating FeCl, Aq to a syrup (8 G c 15), with addition of a little HClAq, and crystallising (Fritzsche, J pr 18, 479, Gobley, J Ph [3] 5, 301, 25, 259) According to Wittstein (R P [2] 36, 30) and Ordway (Z 1866 23), the hydrate thus obtained is FeCl₃ 3H₂O. The hydrate 2FeCl, 5H,O is said to be formed by placing FeCl, 6H,O over H,SO,, the hexahydrate at first liquefies and then loses water —2 With hydrogen chloride and water, to form FeCl, HCl 2H2O thin, transparent, amber yellow laminæ, formed by passing dry HCl gas over 2FeCl, 5H2O, satu rating the liquid thus produced with HCl at 25°, and cooling to 0° (Engel, C R 104, 1708, Sa batier, Bl 1881 197) —3 With ammonia, to form FeCl, NH, When heated, this compound partly sublimes, and is partly decomposed, giving FeCl₂-4 With phosphoric chloride, to form a brown fusible compound, FeCl, PCl, (Weber, J pr 76, 410) -5 With hydrocyanic acid, to form a brown liquid, which then crystallises to FeCl₃ 2HCN (Klein, A 74, 87) —6 With cyano gen chloride, but the compound has not been ob tained pure (v Klein, lc) -7 With nitrosyl chloride, to form FeCl, NOCl, a dark coloured, very deliquescent mass, obtained by placing dry FeCl₃ in the fumes of aqua regia placed over CaCl, (Weber, J pr 89, 152) -8 With alkali chlorides, to form FeCl₃ 2MCl H₂O, M=K, Na, Rb, NH, The NH, compound forms garnet red crystals, by evaporating mixed solutions of the constituent salts The crystals are rhombic according to Fritzsche (J pr 18, 484), dimorphous according to Genth (J pr 71, 164) The double compounds FeCl, 2MCl H₂O are all decomposed by The K salt is described by Fritzsche (J pr 18, 483), the Na salt by Deville (C R 43,970), the Rb salt, said to be FeCl, 3RbCl, by Godeffroy (Ar Ph [3] 9, 343) According to Kremers (J pr 55, 191), a compound of the form FeCl, 2MCl H₂O, in which M is partly K (12 1 pc), partly Na (16 pc), and partly NH, (62 pc), is found in certain volcanic craters -9 With thallium chloride, to form FeCl, 3TlCl (Wöhler a Ahrens, A 144, 250) - 10 With magnessum and berylhum chlorides, to form FeCl, MCl, H₂O, formed by adding MgCl2 or BeCl2 to a cone hot so lution of FeCl, in HClAq (Neumann, A 244, 328) Ferroso ferric chloride Fe₃Cl₃(FeCl₂ 2FeCl₃) When Fe,O, H,O is treated with a little HClAq, FeCl₂ goes into solution, and Fe₂O₃ remains,

porating FeCl, Aq on the water bath, and allow-

but Fe₂O₄ H₂O dissolves wholly in considerable excess of cone HClAq When the solution is cooled and placed in vacuo over H2SO4, yellow crystals of Fe Cl. 18H2O are said to separate (Lefort, C R 69, 179) The crystals are del. quescent, at 50 they lose water, heated to 90° HCl is given off and O absorbed, by warming an aqueous solution of the crystals, FeCl, and FeCl,

are formed.

Iron, cyanides of. No cyanides of iron have been isolated, but ferri- and ferro cyanides are numerous, v vol ii pp 332, 334, 338

Iron, ferricyanide and ferrocyanide of, v

vol 11 pp 334 a 338

Iron, fluurides of Two fluorides of Fe are known, FeF2 and FeF3 The former is produced by dissolving Fe in HFAq, the latter by dissolving Fe,O, xH₂O in HFAq

FERROUS FLUORIDE FeF. Small green crystals of this composition separate from a solution of Fe in HFAq (Scheurer Kestner, A Ch [3] 68, 472) By careful heating, FeF₂ is obtained as a white solid FeF, is urchanged by heat, the hydrate is partly decomposed to HF and Fe₂O, Slightly sol in water, more easily on addition of The double salt FeF, 2KF is a green pp, obtained by adding KF/q to FeSO,Aq, the salts FeF, KF2HO, FeF 2NH,F, and FeF₂ NH₄F 2H₂O are described by Wagner (B 19, 896) The Silicofluoride FeF, Sil, (= FeSiF,) is said to be formed as blue green crystals by

dissolving Fe in H₂SiF₆Aq and crystallising (Wurtz, Dictionnaire, 1 1408)

Ferric fluoride FeF₂ Crystals of the hydrate 2FeF₁ 9H O are obtained by dissolving Fe O₃ xH₂O in HFAq and evaporating, or by oxidising FeF, in HFAq by HNO, The crystals are yellowish according to Berzelius, colourless according to Scheuler Kestner (A. Ch. [3] 68, 472) At 100° 3HO is removed, at higher temperatures H₂O and HF escape By heating the salt died at 100° in a Pt ciucible colourless crystals of FeF, are formed on the surface of the mass, isomor phous with AlF, (Deville, C R 43, 970) Slowly dissolved by water, addition of NH, Aq ppts the Feb forms oxyfluoride 3Fe,O, 2FeF, 4H,O double salts with K, Na, and NH, these are obtained by adding FeF, Aq to solutions of the alkalı fluorides, the salts described are FeF, 3KF (Berzelius, Wagner, B 19 896) FeF, 3KF (Berzeitus, Wagner, B. 17, 670), 2FeF, 4KF HO (Nicklés, Z. 7, 480), FeF, 3NaF (B, W, lc), FeF, 2NaF (Nicklés, J. 1869, 268), FeF, 2NH, F(N, lc), to this salt Manignac gives the formula FeF, 3NH, F(A Ch [3]60, 306) Iron, haloid compounds of Iron readily

combines with the halogens With each halo gen, two compounds are formed, ferrous FeX and ferric FeX3, ferric iodide, however, has not been isolated with certainty, the compound Fe₃Cl₈, corresponding to Fe₃O₄, also perhaps exists. The only compounds that have been gasified are ferrous and ferric chloride former has the molecular formula FeCl, at 1300°-1500°, but there are indications of the possible existence of molecules of Fe,Cl, at lower temperatures, the latter appears to exist as a gas both as Fe₂Cl₈ and FeCl₃ The haloid compounds of Fe are soluble in water, solu tions of FeBr, and FeCl, are decomposed by much water, the compounds all form several double compounds with the chlorides &c of the more positive metals

Iron, hydrides of No definite hydride of Fe has been certainly solated, but there are several indications of the existence of a com Fe heated pound or compounds of Fe and H to redness absorbs about 46 vols H (Deville a Troost, C R 57,965, 59, 102) Electrolytically deposited Fe contains H along with N, CO, and CO. (Lenz, P. Ergänsbd 5, 252, cf Meidinger,

D P J 163, 283, Chandler Roberts, C N 81, 137; Iron wns takes up H when mersed in dilute H₂SO₄Aq (Johnson, Pr 23, 168, Reynolds, C N 29, 118) According to Cailletet (C R 80, 319) Fe npd electrolytically from neutral FeCl,Aq containing NH Cl gives off 235-238 vols H when heated en vacuo Observations on the supposed existence of a gaseous l ydride of Fe were made by Thomson, Dupasquier (C R 14, 511), and Reinsch (J 1858 190) The non existence of such a gas was proved by Fresenius a Schlossberger (A 51, 415) and by Erlenmeyer (N J P 9, 97) Thoma has investigated the conditions under which H is absorbed by Fe (Z P C 3, 91) He finds that when Fe is made the negative electrode in a voltameter, or when it is placed in dilute H2SO, Aq, it absorbs much H, but that Fe a aced in an atmosphere of H does not absorb any of that gas, a certain portion of the H absorbed is given off again on exposure to air or immersion in water, the rest of the H is more firmly retained by the Fe According to Wanklyn a Carius (A 120, 69) when FeI₂ reacts with ZnLt, in presence of ether, various gases including C₂H₄, CH₆, C₄H₁₀, and H are evolved, and a metal like powder remains, which, after washing with ether, is decomposed by HO giving H and a mixture of H and FeO They regard this powder as a hy ride of Fe, perhaps I eH2, but no analyses are given

Iron, hydrated oxides or hydroxides of Compounds with water of each of the three oxides of iron are known. The compositions of the various hydrated oxides are differently represented by different chemists they appear to vary with small changes of conditions, so that it is impossible to say whether all the bodies described are true hydrates or not. The readiness with which most of the hydrated oxides undergo change of composition points to their being hydrates, i.e. compounds of OH. Thomsen (Th. 3, 293) gives the thermal data - [Fe., O', 3HO] = 191,1.0, [2FeO H', O, HO'-54,590, [Fe, O, H'O]=68,280, [FeO H, H SO'Aq]=24,920, [Fe'O'sH'' 3H SO'Aq]=33,840

Only one hydrate of ferrous oride, FeO H O, appears to exist, but it is doubtful whether any hydrate of this oxide has been obtained free from hydrates of le₂O₂. Descriptions are given of two hydrates of ferreso ferric oxide, viz Fe₂O₄ H₂O and Fe₂O₄ 4H₂O, but here again there is great doubt as to the composition of the substances described as definite hydrates Many hydrates of ferric oxide have been obtained, the following are known as minerals $(M = Fe_2O_1)$ M H₂O, M 2H₂O, M 3H₂O, 2M H O, 2M 3H₂O, 8M 5H₂O, the following are said to have been obtained artificially M H₂O, M 2H₂O, M 3H₂O, 2M H₂O, 2M 3H₂O, many of these appear to exist in different modifications each distinguished by special properties, broadly they fall into two classes, those which are insoluble in water, and those which dissolve in water

HYDRATE OF FERROUS OXIDE FeO H₂O The white pp obtained by adding air-free KOHAq to an air free solution of a ferrous salt, and washing out of contact wish air, is probably FeO H₂O To obtain the pp nearly free from ferric oxide Schmidt (A S6, 101) ppts in a closed flask,

allows pp to settle, draws off water by a syphon, carefully pours warm water which has been boiled for some time on to the surface of the cold water in the flask, withdraws water by a syphon, &c , he then quickly transfers the moist pp by a syphon to a retort containing ether, and having attached to it a long glass tube dipping under Hg, the ether covers the pp and drives the air out of the retort, on warming, the water vapour and condensed water escape through the Hg When the ether is removed and the retort is cold, dry air free H (not CO, as the hydrate combines with this gas) is passed through the apparatus, and portions of the solid are transferred in an atmosphere of H to small wide mouthed stoppered tubes Dried in this way, the hydrate is a pale greenish, friable solid, which rapidly oxidises and glows in the air

A de Schulten (C R 109, 266) states that FeO H₂O may be obtained in green six sided flat prisms, which almost instantly become red in air, by mixing 5 grams FeCl₂ dissolved in 100 c c air free water, and 200 c c NaOHAq, containing 20 grams NaOH, in a flask filled with coal gas, heating, and allowing to stand for 24 hours

According to Bineau (C R 41, 509) ferrous hydrate is soluble in c 150,000 parts water Ferrous hydrate is very easily oxidised, it is therefore an energetic reducer, eg it ieduces salts of Au, Ag, and Pt, and also HiO₂Aq It dissolves in acids to foim ferrous salts FeX₂,

$$X = NO_3$$
, $\frac{SO_4}{2}$ $\frac{PO_4}{3}$, &c (cf Ferrous oxide,

under Iron, oxides of)

HYDRATES OF PERROSO FERRIC OXIDE Fe,O, H2O and Fe,O, 4H O, composition of both doubtful Hydrates of Fe,O, are produced by ppg a mixture of equivalent quantities of a ferrous and ferric salt by alkali, and also by digesting ppd Fe₂O₃ xH₂O with Fe The black powder obtained by Wöhler (A 28, 92), by ppg a mixture of equivalent parts of ferrous and ferric sulphates by slight excess of NH,Aq, boiling, washing by decantation, and diving under 100° is said by Lefort (C R 69, 179) to be Fe,O, 4HO By ppg a mixture of equivalent quantities of a ferrous and ferric salt by hot cone kOHAq, Lefort (lc) obtained a hydrate more stable than that got by using NH₃Aq, to this hydrate he gives the formula Fe₃O₄ H₂O The black hydrate obtained by digesting le,O, rH O with Fe under water does not seem to have been analysed (v Preuss, A 26, 96) Ferroso ferric hydrates are described as brown black, magnetic, brittle, powders, when heated out of contact with air they give Fe₃O₄, heated in air, Fe O₃ is produced Ferroso ferric hydrates dissolve in acids to produce mixtures of ferrous and ferric salts, in some cases definite salts of the form Fe₂X₄, $X = SO_4$, &c, are formed, according to Lefort (C R 69, 179) (cf. Ferrosoferric oxide, under Iron, oxides of)

HYDRATES OF FERRIC OXIDE A great many supposed hydrates of Fe₁O₂ have been described, but there is much doubt as to the composition and properties of definite hydrates of the form Fe₂O₂ xH₂O. The following occur as minerals, the compositions of which more or less accurately agree with the formulæ—limonits Fe₂O₂ 2H₂O, Fe₂O₂ 3H₂O, and 2Fe₂O₄ 3H₂O;

gothete Fe_.O_. H_.O_., turgite 2Fe_.O_. H_.O and 3Fe_.O_. 5H_.O According to Ramsay (C J 32, 395), and Brescus (J pr [2] 3, 272), the pp obtained by adding alkali to a ferric salt, either hot or cold, washing, and drying at 100°, is Fe₂O₃ H₂O, by ppg FeCl₂Aq with NH₃Aq, washing first with water and then with alcohol and ether, and drying at 100° the hydrate Fe₂O, 2H₂O is obtained, according to Brescius (*lc*) Witt stein (C C 1853 367) says that the hydrate obtained by ppg a ferric salt by NH, Aq, washing with cold water, and drying at a gentle heat, or at 100° for a short time, is Fe₂O, 3H₂O. The experiments of Carnelley a Walker (C J 53, 89) on the dehydration of ppd Fe₂O₂ xH₂O through a range of temperature showed that the pp after diving at 15° for 18 days contained more water than is required by Fe₂O, 5H₂O, that when heated to 55° the residue had the composition Fe₂O₂ 3H₂O, but that water was gradually and continuously given off from 15° upwards until Fe₂O₃ was formed at 500°, the composition, however, remained constant from 385° to 415°, and corresponded with the formula 10Fe₂O₃ H₂O Van Bemmelen (R T C 7, 106) has examined the composition of the colloidal pp by adding NH, Aq to FeCl, Aq, his experiments, which were very extended, showed the great readiness with which the ratio of Fe₂O₅ to H O varies, e g exposed to air for a year the composition became constant with the ratio Fe₂O₃ 4 or 41H₂O, after 4 months in dry air the ratio was Fe₂O₂ 1 6H₂O, heated to 100° in dry air the ratio was Fe₂O. 96H₂O, the same sample kept for 6 years in a closed flask and then heated to 15° until constant gave Fe₂O₂ H₂O, at 100° Fe₂O₂ 45H₂O, between 100° and 300° the final state was Fe₂O₃ 25H₂O, and so on Besides the papers referred to above on the composition of ppd. Fe,0,xH,0, the following are of im portance —Lefort (J pr 54, 305), P de Saint Gilles (J pr 66, 137), Schaffner (A 51, 177), Muck (Z [2] 4, 41), Davies (C J [2] 4, 69), Tomması (B 12, 1929, 2834)

The monohydrate Fe,O, H,O is said to be obtained (1) by adding NaOHAq and KClOAq to boiling FeSO,Aq, washing, and drying at 100° (Muck, Z [2] 4, 41), (2) by keeping ppd Fe₂O₃ xH₂O in contact with boiling water for 6-8 hours (P de Saint-Gilles, A Ch [3] 46, 47), (3) by repeatedly melting NaOH in a cast iron vessel and washing (Brunck a Græbe, B 13, 725), (4) by keeping ppd Fe₂O₂ xH₂O under water for many years at the ordinary tempera ture (Schiff, C C 1860 1768) This hydrate This hydrate also occurs native as göthite Fe₂O₂ H₂O is described as a dark-red powder, slowly dissolved by dilute warm HClAq, H₂SO₄Aq, or HNO₂, insol in cold cone acids. The mono hydrate obtained by Brunck a Græbe was in the form of small tabular, brownish-violet, hexagonal crystals, S G 2 91 Göthite forms rhombic crystals, SG 38 to 42 The monohydrate obtained by Péan de Saint-Gilles, by keeping Fe₂O₃.xH₂O in contact with boiling water for 6-8 hours, is described as a brick-red powder, scarcely acted on by cone boiling HNO.Aq, slowly dissolved by cone hot HClAq, it dissolves in dilute HNO,Aq, HClAq, or acetic acid, forming a red liquid which appears clear by transmitted, but

turbid by reflected, light, and is ppd by a very smill quantity of an alkal, salt, on addition of cone HNO₂Aq or HClAq, this solution gives a red pp which dissolves on adding water. This modification of Fe₂O₃ H₂O does not form Prus sian blue with K₁FeCy₆ and acetic acid

The dshydrate Fe₁O₂ 2H₂O is said to be obtained by ppg cold Fe₂O₂Aq by NaOHAq and KClOAq or H₂O₂Aq, was 'ing, and drying at 100° (Weltzien, A 138, 125, Muck, lc) This hy-

drate also occurs native as limenite

The hydrates 2Fe,O, H,O and 2Fe,O, 8H,O are said to be formed by the action of water on ppd Fe,O, xH,O, the first by boiling for 100 to 1,000 hours, Davies (C J [2] 4,66), the second by long continued action of water at the ordinary temperature (Wittstein, Ar Ph 74, 158), or, crystalline, by freezing Fe,O, xH,O suspended in water (Limberger, C C 1853 783) By heating any of the hydrates in sealed tubes Fe,O, is eventually produced (Sénarmont, C R 32, 762)

Muck (Z 1868 41) thinks that the ferric hydrates obtained by oxidising ferrous hydrates or carbonate in air differ essentially in properties from the ferric hydrates obtained directly from ferric salts. Tommasi (Bl [2] 38, 152, T a Pellizzari, Bl [2] 37, 196) arranges the ferric hydrates in two classes the red hydrates obtained by present salts by alkali, and the yellow hydrates obtained by oxidising hydrates of FeO or Fe₂O₄, or by oxidising FeCO₂

Ferric hydrates give up 0 to readily oxidised compounds such as SO, Aq, $SnCl_2Aq$, in contact with decaying organic bodies the hydrates part with 0, but again take it up if exposed to air, they absorb gases eg NH₃ and CO_2 (v Rein hart, Fr 7, 187) They dissolve in acids to

form ferric salts FeX_s , $X = NO_s$, $\frac{SO_s}{2}$, $\frac{PO_s}{3}$ &c

These hydrates when freshly ppd also dis solve in FeCl.Aq forming oxychlorides (q v) (v Firric oxide, under Iron, oxides of, p 62)

SOLUBLE FERRIC HYDRATES A modification of Fe₂O₃ H₂O soluble in water was prepared by P de Saint Gilles in 1855 (A Ch [3] 46, 47) Ordinary ppd Fe,O, xH,O is dissolved in acetic acid, the solution is heated to 100° for a long time in a closed vessel, the blood red colour of the liquid changes to brick red, the liquid appears opalescent in reflected light, and the taste is no longer metallic but merely that of acetic acid, on now adding cone HClAq or HNO, Aq, or the merest trace of H2SO4Aq or an alkalı salt, the whole of the Fe is thrown down as a brown red curdy pp, which, when dried on a porous tile, appears as a brown, lustrous, /arnish like solid, having the composition Fe₂O₃ H₂O This modi heation of ferric hydrate, sometimes called ferric metahydrate, is insol in conc acids, but dissolves easily in water, forming a deep-yellow, opalescent, tasteless liquid, unchanged by K,FeOy, or KCNS Traces of H,SO, or alkalı salts, and also cone HClAq or HNO, A, ppt the hydrate from its aqueous solution. The same hydrate has been obtained by Scheurer Kestner by prolonged heating an aqueous solution of basic ferric nitrate in a realed tube at 100° (C R 48, 1160), also by Debray by heating dilute FeCl.Aq to 100° (C. R 68, 913, cf. Ferric chloride, Reactions, No 4, p 55) Another soluble modification of ferric hydrate, some ames called dialysed oil colloudal ferric hydrate, is obtained by dialysing a solution of FeČl, containing Fe $_{\circ}$ O, xH $_{\circ}$ O so long as the dialysate contains HCl (Graham, Tr 1861 183) The solution is prepared by digesting FeCl₂Aq with ppd Fe₂O₃ xH₂O, or by adding (NH₄),CO,Aq to FeCl,Aq so long as the pp dissolves on stirring, the solution should contain 4-5 p c of solid matter, and have 5-6 equivalents of ferric hydrate in it After dialysis a deep red liquid is left on the dialyser, this liquid gelatimises by exposure to the air for some days or by traces of H,SO,, alkalis, alkaline salts, but not by HCl, HNO,, or acetic acid, the jelly like mass thus outsined slowly becomes insol in water, and is then sol in dilute acids, it appears to be changed to the ordinary Fe₂O₂ xH₂O (Graham *l.c*, of Shuttleworth, *Ph* [3] 8, 545, Bec querel, A 126, 208)

Krecke (J pr [2] 3, 286) has examined the formation of soluble ferric hydrates from FeCl.Aq Formation of the colloidal hydrate occurs in FeCl, Aq cortaining $\frac{1}{10}$ to $\frac{1}{8}$ p c FeCl, at ordinary temperatures, solutions containing 8 to 32 p c must be heated to above 100° in closed tubes, on cooling the more conc solutions (if not heated too long and too highly) re formation of FeCl, occurs, but in solutions of less than 1 pc the base and acid remain uncombined ca cooling a solution containing less than 1 pc is boiled for some time formation of ferric metahy drate begins, and after a time the hydrate is ppd as an orange yellow powder A table showing the various products obtained by heating solutions of FeCl. Aq of different concentrations to different temperatures is given under Ferric chloride, Reactions, No 4 (p 55)

Iron, lodides of Only one iodide of iron,

Fel, has been isolated with certainty

FFRROUS HODIDF (Proto nodule of aron) Fel, **HF** $[Fe, I^2, Aq] = 47,650 (Th 3, 294)$ Fe and I combine by rubbing together with or without water, Fe and I heated together form a crystal line grey mai 3 which melts at 177° (Carius a Wanklyn, A 120, 69) According to De Luca FeI₂ is white, but goes green on addition of water $(C \mid R \mid 55, 615)$ Green deliquescent water (C R 55, 615) Green deliquescent crystals of FeI₂ 5H₂O, S G 2873, are obtained by digesting I part Fe filings with 3 4 parts I in presence of water, adding Fe filings, evaporating ΓeI₂, out of contact with air, and filtering especially Fel2Aq, rapidly absorbs O with formation of oxylodide $(q \ v)$ Addition of sugar syrup to FeL renders the solution more stable H₂O₂Aq decomposes FeI₂ with formation of Fe,O,xH,O and separation of all the I Fel,Aq dissolves I, addition of K₂CO, to a solution containing 3FeI₂ 2I forms KI and Fe₂O₄.xH₂O, the solution may contain Fe,I,

FERRIC TODIDE (?Fel,) This iodide has not been isolated, it is probably contained in a solution of FeI, to which I is added in the ratio Fel, I. Fel, Aq containing I is separated by heating to FeL and free I Fleury (J Ph [5] '16, 529) says that the action of I on Fe in presence of water soon ceases if the temperature is kept down to 15°, on filtering, only Re is obtained, if, however, the mixture is Boiled the red colour of the liquid disappears and a considerable quantity of Fe₂O₂ is found in the re-

sidue A large excess of I is required to dissolve all the Fe, and a large excess of Fe is required to'convert all the I into FeI, F sup. poses that FeI, is at first formed and is then decomposed by the heat to Fe₂O₂ and HI, and the HI then acts on the free Fe forming FeI. Mohr observed that a very dilute solution of FeCl, (1 in 12,300) gives a blue colour on addi tion of starch and KI only after a considerable time (A 105, 53) Nickles found that a solu tion of Fe O, xH2O in HIAq in presence of ether did not at once give a blue pp with K.FeCy. (A Ch [4] 5, 161, cf Ordway, Am. S [2] 26, A solution made by digesting 126 parts I 197) with sufficient iron, filtering, and adding 63 parts I, gives an apple green pp on addition of 201 parts citric acid previously neutralised by alkali carbonate (Creuse, Ph [3] 3, 953) According to Carius a Wanklyn (A 120, 70) if Fe is heated According with excess of I until a little I is vaporised, and the mass is allowed to cool in a covered crucible. I is suddenly evolved, and the residue consists of

Iron, nitrides of A nitride of Fe, Fe, N, is found as a silver like lustrous deposit in the lavas of Ltna (Silvestri, P 157, 165), heated in H it yields Fe and NH, Finely divided Fe, prepared by heating ferrous oxalate or reducing Fe O, by H, takes up about 2 pc N when heated in N (Geuther a Brieglet, A 133, 228, Rogstadius, J pr 86, 307, Remsen, Am 3, 134) By heating Fe in NH, the Fe increases in weight 12-13 pc and becomes brittle (Berthollet, G A 30, 378) By electrolysing a mixture of NH₂Cl and a ferrous salt a lustrous deposit is obtained, supposed by Kramer to be a nitride of Fe with 15 pc N (Ar Ph [2] 105, 284), but said by Meidinger (D P J 163, 283) to be an Fe NH. A nitride (or nitrides) of iron seems amalgam to be produced by heating FeCl, or FeCl, in NH, The product is a brittle, grey white, solid, heated alone it gives N and Fe, heated in H it gives NH, and Fe, it is slowly and partially decomposed by boiling water, in acids with formation of H, ferrous and NH, salts, not acted on by Cl, Br, or I in presence of HO at ordinary temperatures, but when heated ferric and NH, salts are formed, and H, and probably also N, are evolved The formula Fe,N, agrees with most of the analyses, the forraula Fe, N, was given by Stahlschmidt (P. 125, 37, cf Rogstadius, J pr 86, 307, Fremy, C R 52, 321)

Iron, nitroprusside of, v vol. 11 p 340 Iron, nitrosulphides or nitrososulphides of. In 1858 Roussin obtained a salt by the reaction of NH.HS and KNO₂ on FeCl.Aq, which contained Fe, but in which Fe could not be detected by the ordinary tests (A Ch [3] 52, 285) Proczinsky (A 125, 302) obtained the same compound by adding NH, HS to a solution of a ferrous salt saturated with NO A similar salt was obtained by Pavel by using K2S in place of NH, HS (B 12, 1407) By treating these salts with alkali others were obtained more or less closely related to the original salts The compounds thus obtained were analysed and examined by Roussin (lc), Proczinsky (lc), Rosenberg (B 8, 812, 12, 1715), Demei (B 12, 461), and Pavel (B 12, 1407, 1949, 15, 2600) Roussin's analyses of the compound formed by using

NH₄HS led to the formula Fe₃S₃H₂(NO)₄, to the same compound Proczinsky gave the formula Fe₂S₃(NO), 2H₂O, and Rosenberg assigned the composition Fe₂S₁(NO), 4H₂O In his second paper R showed that the compound prepared by using K2S contained K, this was confirmed by All the observers admitted the presence

of the NO group in these compounds Pavel (B 15, 2600) has given an account of the compounds of which Roussin's salt is the type, and has indicated what appear to be their relations to other compounds of iron As the compounds contain the group NO in addition to S they are better called nitroso than nitrosulphides Pavel regards the nitroso sulphides of Fe as salts of acids, the acidic radicles of which are composed of Fe, NO, and S, the salts may be formulated generally as derived from the acids $\mathbf{H}_{w}\mathbf{Fe}_{x}(\mathbf{NO})_{y}\mathbf{S}_{z}$ P compares the ferrontroso sulphides with the ferronitrosocyanides or nitroprussides, which are salts of H, Fe(NO)Cy, (v Nitroprussides, vol 11 p 340) According to P there are two series of ferronitroso sulphides derived from the two acids HFe, (NO), S, (or $H_2Fe_s(NO)_{14}S_s$), and $HFe(NO)_2S$ (or $H_2Fe_2(NO)_4S_2$) The former acid has been isolated, the latter is not as yet known in the The two series may perhaps be called ferrinitroso and ferronitroso sulphides In the following account of the salts Pavel's formulæ are adopted -

Series I Ferrinitrososulphides

M'Fe (NO) S.

Potassium ferrinitrososulphide KFe, (NO) S, A solution of KHS, made from 44 grams KOH in 400 cc water, is added to a boiling solution of 35 grams pure NaNO2 in 400 cc water, the mix ture is heated just to boiling, and a solution of 159 grams ferrous sulphate in 1200 cc water, to which a drop of dilute H,SO,Aq has been added, is allowed to flow into it with constant stirring, the liquid is kept warm on a water bath, and is shaken from time to time until a greenish red pp (of Fe₂O₃, FeO, and S) forms on the sides of the flask, when the liquid is rapidly filtered, a little dilute KOHAq is added to it when cold, and it is allowed to stand for 48 hours The salt which separates is dissolved in water at 70°, a little KOHAq is added as the liquid cools, and the crystals thus obtained are recrystallised in the same way, after standing 48 hours; the crystals are then dried over H,SO, in vacuo pro tected from the light About 30 grams of the pure salt are thus obtained (Pavel, B 15, 2601) If more KHS is used than directed above double sulphides of Fe and K are obtained and no nitrososulphide

KFe (NO), S, crystallises in large, nearly black, lustrous, rhombic prisms, it is fairly stable in the air, decomposition begins at c 115° with evolution of NO, at c 130°S, (NH₄)₂SO₄, NH₄NO₅, &c , sublime , heated in air H₂O, NO₅, N, SO₅ are evolved, and the residue consists of FeS, Fe,O,, Fe₂Q₃, and K₂SO₄, strong mineral acids evolve H₂S Various metallic salts form metallic sulphides and NO, while Fe salts remain in solution, heated with alkali, crystalline Fe₂O₂ is ppd, NO evolved, and ferronitrososulphide KFe(NO), S is formed (Pavel, lc) KFe4(NO),S1 is soluble in about 2 parts hot water, slightly sol in cold water, very sol with decomposition (Pavel, B.

12, 1410) in alcohol or ether, the salt is ppd by The talts of this series do NI Aq or KOHAq not react with K.FeCy.

The following salts of this series have been isolated NH,X, BaX, CsX (the most stable salt of the series), CaX_2 , FeX_2 , L_1X , MgX_2 , RbX, TlX (X = $Fe_1(NO)_2S_3$) The Na salt is formed similarly to the K salt, also by the reaction of Na₂CS with NaNO2, the comp und Fe4S(NO)6 CS, said by Low (C C 1865 \$48) to be formed in this reaction does not exist according to Pavel (B 15, 2603) For other reactions of the salts of the series v Pavel, B 15, 2604

Ferriniti ososul phydi w acid HFe,(NO),8, seems to be obtained by adding a slight excess of dilute H, SO, Aq to a dilute solution of the Na salt, it is insol in water, alcohol, and ether, The acid has not been sol in CHCl₃ or CS

obtained pure (P, lc)

Ferronitrososulphides Series II MIFe(NO), S These salts are formed by the action of dilute alkali solutions on the salts of Series I . in these reactions NO is evolved and Fe O, ppd, but NH, is not evolved except from the salt NH, Fe, (NO), S, The salts of Series II are very unstable, they easily pass into Series I, the Cs salt is the most unstable of all, these salts are insol in ether (except the Fe salt), CS, and CHCl3, they decompose in the air with separa tion of S and Fe₂O₃ and evolution of a little H S, the solutions then have an alkaline reaction, and contain salts of Series I along with alkaline ni trite and thiosulphate If CO is passed into a solution of K₃ FeCy, and the K salt of Series II is then added, NO is evolved, S and Prussian blue are ppd, and the filtrate contains k, FeCy. and some KNO

Potassium ferronitrososulphide KFe(NO)2S 2H2O is obtained by warming KFe,(NO),S, on the water bath with dilute KOHAq, washing, and drying in vacuo over H SO, and CaO in the dark, it is very unstable, and can be obtained approximately pure only with difficulty (P, B 15, 2606) By warning an alcoholic solution of KFe(NO)₂S with considerable excess of EtI, quickly distilling, washing the re sidue first with water and then with aqueous al cohol, and crystallising from benzene, ethyl fer ronitrososulphide (C2H2)Fe(NO)2S is obtained in black, lustrous, monoclinic crystals (P, lc) For a discussion of the probable constitution of these nitrososulphides and a comparison of them with

the nitroprussides t Pavel, B 15, 2613

Iron, oxides of Three oxides of iron have been isolated, FeO, Fe₂O₄, and Fe₂O₃ The molecular weight of none is known with certainty, as none has been gasified FeO and Fe₂O, are basic oxides, they produce salts by reactions with acids, of the forms FeX_2 and FeX_3 , X = Cl, NO_3 ,

 $\frac{SO_4}{2}$, $\frac{PO_4}{3}$, &c , Fe₂O₅ also combines with some

more positive metallic oxides to form compounds Fe₂O₃ xM¹¹O, which are usually called ferrites (v vol 11 p 547) Fe₈O₄ eacts with acids to form both ferrous and ferric salts, FeX2 and FeX4, according to Lefort a few salts corresponding with Fe₂O₄ are known, eg Fe₂Cl₁, Fe₂(SO₄), 2SO₂ 15H₂O (v Ferroso ferric oxide, p 61) Besides the ferrites a series of ferrates is known (v. vol. 11 p 546), these salts are of

the form MI, FeO, , they may be regarded as salts of the hypothetical ferric acid H₂FeO₄, the anhydride of this soid would be FeO, this oxide of iron has not been isolated, but the corresponding oxide of Mn, MnO₂, is known All the oxides of Fe form hydrates (v Iron, hydrated oxides of, FeO very readily and rapidly absorbs O and changes to Fe₂O₁, at a very high tempe rature Fe₂O₂ parts with O, and is reduced to Fe,O,

FERROUS OXIDE (Protoxide of iron) FeO This oxide cannot be obtained free from Fe₂O₃ by ppn from ferrous salts and dehydrating the

Preparation -1 Pure Fe₂O₃ is heated to c 300° in a stream of pure H (Wackenroder a Stromeyer, Ar Ph 36, 27) -2 By heating fer rous oxalate out of contact with air (Liebig, A 95, 116, Moissan, A Ch [5] 21, 199) -3 By heati g Γ e O₃ for 20 minutes to c 500° in H or CO, or in CO at 440° for 6 hours (Moissan, lc) 4 By heating Fe in CO₂ to c 1000° (Moissan, lc) -5 By adding ferrous oxalate to boiling KOHAq (Bottger, J pr 76, 239)
Properties and Reactions -An ivory black

powder According to Moissan (lc) FeO ob tained by heating ferrous oxalate, or reducing Fe.O. in CO at 500°, is pyrophoric, burns to Fe O2, and decomposes water at ordinary tem peratures, while the FeO obtained by heating I e in CO2 at c 1000° is non pyropheric, burns to Fe₃O₄, and does not decompose water at 100° Siewert (J 1864 266) says that pyrophoric FeO, produced by reduction of he,O, in H, becomes non pyrophoric by remaining in an atmosphere of H for 12 hours after cooling FeO is readily oxidised to Fe₂O₂ (cf Moissan, supra) It dis solves in acids to form ferrous salts FeX2, X = Cl,

$$NO_3$$
, $\frac{SO_4}{2}$, c

Combinations — The compound FeO Al.O.oc curs native as hercynite, and FeO Cr2O, as chrome ironstone, magnetic oxide of iron may be regarded as FeO Fe₂O₃ The hydrate FeO H₂O has been 180 sted (v Hydrate of ferrous oxide, p 57)

FERROSO FERRIC OXIDE (Black or magnetic oxide of iron) Fe,O, This oxide occurs native in large quantities as magnetite According to Spring (Bl [2] 50, 215) it is produced on the surface of iron which has been subjected to great pressure, the formation of a film of this oxide on iron rails is the reason why the surfaces of the rails of railroads do not rust (Spring, lc) When iron is strongly heated in air a film (hammer scale) is produced consisting of Fe,O, mixed with, or combined with, ke2O1, the outer layer of this film contains a large quantity of Fe O₂, the inner layer, which is blackish grey and magnetic, is approximately 6FeO Fe,0, (Mosander, P 6, 35, cf Berthier, A Ch [2] 27, 19, Beaujen a Mène, C R 61, 1135, Maumené, Bl 16, 25, Völcker, W A B 66, 193, Glasson, A 62, 89) 8 G 5 458 (Playlair a. Joule, C S Mem 3, 81), 5 8 at 16 5° (Herapath, P M 64, 321) S G of magnetate 5 1 to 5 18 (Kopp, Rammelsberg) According to Moissan (A Ch [5] 21, 223) two varieties of Fe₁O₄ exist, one having S G 4 86 obtained by reducing Fe₂O₄ at 500°, the other having 5 135 (Playfair a Joule, C S Mem 3, 80), ppd. S G 5 18 obtained by reducing Fe₂O₄ at a higher 5 959 at 16 5° (Herapath, P M 64, 321) S.H.

temperature Berthelot (A Ch [5] 23, 118) describes two varieties, one with S G 4 86 obtained by heating FeCO, to 350°, the other with SG 5-59 obtained by highly heating the first in N. Magnetite crystallises in regular octahedra, isomorphous with Mn,O, (Rammelsberg) CE, 000029 (Kopp) SH 24°-99° 16779 (Regnault, A Ch [3] 1, 129) HF [Fe³,O¹] = 26,900. $[FeO, Fe^2O^3] = 8,800$ (Berthelot, A Ch [5] 23.

Preparation -1 By heating FeCO, to c 350° in a current of CO₂ (Berthelot, A Ch [5] 23 118) -2 By heating FeCl₂2NH₂Cl in air (Hauer, W A B 13, 456) -3 By heating FeO in a gentle stream of HCl (Deville, C R 53, 199) -By melting ferric phosphate with 3-4 pts. Na. SO, (Debray, C R 52, 985) -5 By melting CaCl₂ with ferrous sulphate in a closed crucible (Kuhlmann, C R 52, 1283) -6 By the action of FeF_s on borne and at a high temperature in absence of air (Deville a Caron, A 108, 56) -7 By heating FeCl₂ with excess of Na₂CO₂ to low redness and washing with water (Liebig a Wohler, P 21, 582) -8 By heating Fe in steam 9 By long continued heating Fe₂O, to white-heat (Sidot, C R 69, 201) -10 By reducing Fe,O, in CO at 350° for about an hour (Moissan, A Ch [5] 21, 223, cf Birnie, R T C 2, 273, Ackermann a Sarnstrom, B 16, 783) -11 By dehydrating Fe₁O₄ xH₂O at as low a temperature as possible (v Hydrates of ferroso ferric oxide, p 57)

Properties and Reactions - A black, magne tic powder, the crystals obtained by methods 4-7 (supra) are black octahedra According to Moissan (A Ch [5] 21, 223) and Berthelot (A Ch [5] 23, 118), Fe₄O₄ obtained by heating FeCO₂ in CO₂ at 350°, or by reducing Fe₂O, by CO at 350°, or by heating reduced Fe in H saturated with H2O, or in CO, at 440°, has a lower SG than Fe,O4 produced by reductions at higher temperatures, or by strongly heating the first variety in N, the first variety is said to be easily soluble in conc HNO, Aq, and to give Fe,O, when heated on Pt foil, the second variety is described as almost unacted on by boiling conc HNO, Aq and as un changed to Fe₂O, by heat Fe₃O, is reduced to Fe by heating with C, or by strongly heating in With a little HClAq it gives FeCl, Aq and Fe₂O₂, with more HClAq it gives a solution showing the reactions of both ferrous and ferrie chloride According to Lefort (C R 69, 179) Fe₂Cl₂ is obtained by cooling a solution of Fe,O, xH,O in excess of conc HClAq and evaporating in accuo over H.SO. (1 Ferroso ferric chloride, p 56) Lefort (l.c.) also describes a ferroso ferric sulphate -Fe, O, 6SO, 15H2O-obtained by evaporating, over H SO, solutions of Fe₂O₄ in H₂SO₄, he says that arsenates and phosphates of Fe₃O, also exist, the solutions of these salts are decomposed to a mixture of ferrous and ferric salts by warming to 60°-70° (for hyrates of Fe₂O₄ v. Hydrates of ferroso-ferric oxide, p 57)

(Peroxide, sesquioxide, or) Fe.O. Occurs native in FERRIC OXIDE brown oxide, of iron) Fe₂O, large quantities widely distributed as red hæmaute, specular iron ore, and martite 8 G native 15°-98° ·16695 (Regnault, A Ch [8] 1, 129) CE 00004 (Kopp) Crystallises in hexagonal forms, a c = 1.186537 (Rammelsberg)

Preparation —1. By ppg a ferric salt by NH₂Aq, thoroughly washing, and strongly heating the pp -2 By strongly heating ferrous exalate in air, Vogel $(J \ pr \ 63, \ 187)$ says this method gives a very pure product —3 By heating ferrous carbonate in air —4 By strongly heating ferrous sulphate in air, the product seems always to contain a little basic sulphate unless the temperature is kept very high for a long time

The oxide is obtained in crystals by the following methods -5 By heating a mixture of equal parts ferrous sulphate and NaCl, and washing with water, the temperature must not be too high, else some Fe₃O₄ is produced —6 By heating Fe₂O₃ in a slow stream of HCl gas (Deville, O R 52, 1364), in a rapid current of HCl, FeCl₃ is produced —7 By melting Fe₂O₃ with CaCl₂ (Kuhlmann, C R 52, 1283) —8 By the action of FeCl, vapour on strongly-heated lime (Daubré, C R 49, 143) —9 By melting Fe₂O₃ with borax and treating the fused mass with warm dilute HClAq (Hauer, W. A B 13,

Properties - A reddish-brown, very hard, non magnetic powder, extremely hygroscopic, slightly volatile at c 3000° (Elsner, J pr 99, 257) According to Malaguti a magnetic variety of Fe,O, exists (A Ch [8] 69,214, cf Lallemand, A Ch [3] 69, 233, Lawrence Smith, B 8, 183)

Reactions -1 Heated to a very high temperature Fe₂O₃ is partially deoxidised to Fe₃O₄ (Sidot, C R 69, 201) —2 Reduced by heating in hydrogen, according to Moissan (C R 74, 1296) Fe₂O₃ (prepared from ferrous oxalate) is reduced to Fe₃O₄ by heating to 350° for an hour in H, reduced to FeO by heating to 500° for 20 minutes in H, and to Fe when heated in H at 700° (cf Siewert, J 1864 265) Wright a Luff (C J 33, 1) found that the temperature at which reduction of Fe₂O, by H begins varies from 195° reduction of re₂O₃ by In begins value and are to 260° according to the physical state of the Fe₂O₃ used --3 Reduced by heating in carbon monoxide, to Fe₃O₄ at 350°, to FeO at 500°, and to Fe at 700°-800° (M, Ic, cf Gruner, CR 73, 28) Temperature at which reduction begins varies from 90° to 220° according to physical state of Fe₂O₃ used (W a L, lc)—4 Reduced by heating with carbon to Fe₃O₄, and then to Fe which combines with part of the C (v Iron, carbides of, p 53) Reduction begins at 430°-450° (W a L, lc) According to Parry (C N 27, 313) reduction of Fe₂O, by C in a vacuum begins at above 400°, at 1200° c 3 of the oxide is reduced.—5 Reduced to FeO by heating in a mixture of equal volumes of carbon monoxide and dioxide (Debray, C R 45, 1018) -6 A mixture of carbon dioxide and cyanogen (6 vols partially reduces Fe₂O₃ to Fe at c 600°-700° (Bell, J. 1874 266)—7 Heated in ammona Fe₂N₃ is produced (v Iron, nitrides of, p 59) 8 Chlorine forms FeCl, slowly at full red heat (Weber, P 112, 619)—9 Heated with sulphur 80, and FeS are produced (Brescuus, D P J 192, 125).—10 Heated strongly in a rapid stream of hydrogen chloride FeCl, and H,O are formed (Deville, C R 52, 1264) -11 Sulphuretted hydrogen does not act on dry Fe,O,; with

moist Fe₂O₂ (Fe₂O, xH₂O) FeS, S, and H₂O are formed (Wright, C J. 43, 156, Brescius, D P J 192 125)—12 Phosphor c chloride produces FeCl, which then combines with part of the PCl, forming FeCl, PCl, (Weber, J pr 76, 410) -18
Fe₂O₃ is slowly dissolved by acids, the more slowly the denser the specimen of Fe₂O₃, most easily dissolved by 16 times its weight of a boiling mixture of 5 pts H₂SO, and 3 pts H₂O (Mitscherlich, *J pr* 8¹ 108) After strongly heating with alkalis, alkaline carbonates, or acid sulphates, Fe₂O₃ is readily dissolved by acids -14 Fe O, readily parts with O when heated with oxidisable organic compounds, on exposure to air O is again taken up (Robin, C R 49, 500, Grager, A 111, 124) Moist Fe,O, (Fe₂O₂ xH₂O) in presence of ordinary air serves as an oxidiser of various vegetable matters, e g wood (Kuhlmann, D P J 155, 31, cf. P Thénard, C R 49, 289)

Combinations -1 Fe₂O₃ is extremely hygro scopic, it forms several hydrates by combining with water For conditions of formation, composition, and properties v Hydrates of ferric oxide, p 57—2 With some more ositive me-tallic oxides to form ferrites (q v in vol 11 p 547)

HYPOTHETICAL FERRIC ANHYDRIDE (? FeO.) This oxide has not been isolated, but a number of salts are known, which are best regarded as derived from the hypothetical acid H, FeO, of which FeO, would be the anhydride These salts are described under the heading Ferrates (vol 11 p 546) In addition to the descriptions there given it is to be noted that when air is blown into hot cone NaOHAq containing c 34 pc NaOH, a perceptible quantity of Fe is dis solved to form a colourless liquid, from which Fe₂O, xH₂O slowly separates (Zirnité, Chem Zeitung, 12, 355), possibly the solution con tains a ferrate of Na, or, according to the sug gestion of Z, a perferrate NaFeO, (?)

Iron, oxybromides of Oxybromides of Fe are said to be formed by evaporating FeBr,Aq, and by the action of Fe₂O₃xH₂O on FeBr₁Aq or HBrAq (Ordway, J pr 76, 19, Bcchamp, A Ch [3] 57, 296, Scheufelen, A 231, 1'7)

Iron, oxychlorides of The oxychlorides of

Fe are numerous and of complex composition, they belong to the form xFeCl, yFe,O, zH2O They are divided into two classes, those which are soluble in water, and those which are in soluble

Soluble oxychlorides Prepared by di gesting freshly ppd Fe₂O₂xH₂O in FeOl Aq, also by digesting excess of Fe₂O₃xH₂O in HclAq By the former method Ordway obtained 2FeOl₂28Fe₂O₃ (J pr 76, 19) By the second method Bechamp (A Ch [3] 51, 296) obtained liquids containing FeCl, and FeO, in ratio 25, 13, 14, and 15 All these solutions evaporated at c 40° give residues soluble in water, solutions containing more Fe₂O₃ than the foregoing (up to 10Fe₂O₃) give residues on evaporation which are insol in water Solutions of soluble oxychlorides are not decomposed by dilution or heating, but addition of various acids and salts causes ppn. of Fe₂O₂ xH₂O, mixed with oxychlorides, which are soluble in water From solutions of soluble oxychlorides NH, Aq ppts Fe₂O, xH₂O free from chloride, whereas the pp obtained from the insol oxychlorides contains chloride

Insoluble oxychlorides Prepared by exidation of FeCl2Aq, by exposure to air or by HNO, in presence of a little HCl (Béchamp, la) I o saturated FeCl, Aq, HCl is added in less propor tion than 3HCl to FeCl,, the solution is heated to 100°, and HNO, Aq is graduall, added, a violent reaction occurs, the nearly black liquid becomes yellow, and oxychlorides separate which are insol in water The composition of these exychlorides varies acco ding to the tempera ture and the proportion of HCl used Insol oxychlorides are a so formed by adding alkali to FeCl.Aq in quantity insufficient for complete ppn These oxychlorides vary in colour fro n yellow to brown, they are slowly soluble in HClAq, when heated they lose HO and HCl

Iron, exyfluoride of B adding NH,Aq to a solution of FeF, a yellow salt of the composition 2FeF, 3Fe,O, 4H,O is obtained (Deville, A Ch 13 149, 85)

Iron, oxysulphide of According to Ram melsberg (P 121, 339) the product obtained by heating Fe₂O₂ in H₂S gas to near redness is 3Fe₂S₄ Fe₂O₃

Iron, reduced Ferrum redactum Very finely divided Fe is obtained by reducing Fe O, in a stream of pure H Reduced iron is very readily oxidised, commercial specimens generally contain 40 p c or more of oxide

Iron, phosphides of Meyer ir 1780, and Bergmann somewhat later, obtained a phosphide of 1 e, supposing it to be a new metal they called it Hydrosiderim (Berl Ges d naturforsch Freunde [1781] 2, 334, Bergmann's Opusc 3, 109) Several 1 e phosphides have been described According to 1 reese (P 132, 225) only three exist, I e,P, heP, and Fe,P. They are non magnetic and almost infusible, unchanged by cold HClAq, slowly acted on by boiling HClAq giving \(\frac{1}{2}\) of their P as phosphoric acid and \(\frac{2}{2}\) as BH, oxidised at ordinary temperature by HNO, and uqua regia

Fe₂P₄ By heating FeS₂ in PH₃ gas (H Rose, P 6, 212, 24, 333), also by heating reduced Fe or I cCl₂ in PH₄ (Freese lc) \(\lambda\) blue grey powder, S G 504, loses P by heating in H or CO, probably forming FeP

FeP By heating FeS in PH, for a long time (Freese, lc), also by passing a mixture of H and P vapour over strongly heated Fe₂O₄, and by the action of PH, on FeCl₂(H Rose, l.c) A black crystalline mass, not acted on by HNO₂ or HClAq, nor by I

Fe.P / parts dry FePO, with 1 part lamp black are covered with a layer of NaCl and heated to whiteness, and the fused mass is treated with HClAq, Fe P remains as a grey crystalline solid, S G 574, unchanged by heating in H, CO, or CO₂ (Freese, lc)

The following phosphides have been described in addition to those mentioned, according to Freese they are not definite compounds—Fe,P (Hvoslef, A 100, 99), Fe,P, (Schenk, C J [2] 11, 826), Fe,P, (Struve, J pr 79, 321), FeP, (Sidot, C R 74, 1425)

Iron, salts of Two series of Fe salts, obtained by replacing H of acids by Fe, are known, ferrous salts FeX, and ferric salts FeX, $(X - Cl, 4c., NO_s, 4c., \frac{SO_s}{2}, 4c., \frac{PO_s}{3}, 4c.)$. The ferric

salts are the more stable, as a class ferrous salts are readily oxidised to FeX. Both series contain many well marked and very definite compounds Lefort (C R 69, 179) asserts the ex istence of a few salts, eg chloride, sulphate, phosphate, corresponding to Fe₂O₄ (v Ferrosoferric oxide, p 61) Ferrous salts are usually obtained by dissolving Fe in various acids, or in the cases of the insol salts by double decompo sition from FeSO,, they are for the most part sol in water, a few basic ferrous salts are known. but the greater number are normal salts Many double ferrous salts, especially with the alkali sulphates, have been isolated, many ferrous salts are isomorphous with the corresponding salts of Co, N1, Mn, Zn, and Mg A double ferrous alu minium sulphate, FeSO, Al, 3SO, 24H,O, is said to exist and to be isomorphous with the alums Ferric salts are generally prepared by dissolving Fe₂O₄ xH₂O in the different acids, many basic, and numerous double, ferric salts are known, the double salt (NH,)2SO, Fe (SO,), 24H,O be The ferric salts are longs to the class of alums generally analogous to the persalts of Al, Cr, Co, Ni, and Mn (cf Iron GROUP OF ELEMENTS) following list comprises the more important salts of Fe derived from oxyacids, for details t CAR BONATES, NITRATES, SULPHATES, &C antimonates, arsenates and ites, borates, bromates, carbonates, chlorates, chromates, hypophosphite, iodates, molybdates, niobates, nitrates, perchlorates periodates, phosphates and ites, selenates and -ites, silicates, sulphates and -ites, tantalates, tellurates and ites, thiosulphates, titanates, tungstates, vanadates

Iron, selemides of Selemides of Fe seem to be obtained (1) by passing Se vapour over strongly heated Fe, (2) by heating the product obtained in (1) with Se (Berzelius), (3) by method (2) covering the mass with borax, Little (A 112, 211) obtained Fe,Se, thus, SG 638, (4) by ppg Fe salts by H,Se (Reeb, J Ph [4 9, 173) By heating Fe filings with Se to it liness Divers a Shimidzu (C J 47, 441) obtained FeSe, resembling FeS in appearance, with acids yields H.Se

Iron, selenocyanides of None has been iso lated, Crookes (C J 4, 12) mentions various reactions which do not yield a definite salt

Iron, silicide of It is doubtful whether any definite compound has been isolated Silicides are apparently formed (1) by heating Fe with Si (Deville a Caron, C R 45, 163), (2) by the action of molten Fe on silicates Hahn (A 129, 57) obtained a body approximately Fe,Si by fusing 60 parts Na. Sile,, 20 parts Na, 60 parta Zn, and 22 parts steel, under NaCl Other bodies, approximately Fe Si and Fe, Si, are described by Deville a Caron (lc) and Hahn (lc, ct Bous singuilt, A Ch [3] 16, 15)

Iron, silicofluoride of, FeSiF, v Ferrous fluoride, p 56

Iron, sulphoeyanides of, v vol 11 p 350 Iron, sulphides of Four are known, FeS, Fe,S., Fe,S., and FeS., a subsulphide, Fe,S. also probably exists According to Gautier a Hallo peau (C R 108, 806) a yellow grey lustrous body, Fe S., 1s formed by heating Fe in CS. for several hours at 1300°-1400°

IRON SUBSULPHIDE Fe.S Said by Arfvedson (P. 1, 72) to be produced, as a greyish-black powder, by heating dry FeSO₄ in H.

or protosulphide) Occurs sometimes in meteor-

ites, also in combination with NiS

Formation - 1 By heating FeS₂ with Fe until the mass is thoroughly molten - 2 By reducing FeS₂ in H - 3 By the reduction of Fe₂O₃ or ferric salts by decomposing organic matter in presence of sulphates (Chevreul, C R 43, 218) 4 By gently heating a mixture 1 part S with 13 parts Fe filings moistened with water, if a con siderable quantity of such a mixture is made into a paste with water and covered with earth, the mass after a time becomes red hot and evolves much steam which throws up the earth with some violence—5 By strongly heating Fe₂O₃ or a ferric salt in H₂S (Sidot, C R 66, 1257, cf Carnot, Bl [2] 32, 162) - 6 By heating a mixture of Fe₂O₂ and S in H (Rose, P 110, 120) -7 By heating to redness a mixture of Fe₂O₃ and excess of Na₂S₂O₃ (Gibbs, Am S [2] 87, 346)

Preparation -1 A mixture of 8 parts Fe filings and 2 parts S is strongly heated in a covered crucible until the whole mass is thoroughly melted, if the temperature is not high enough some Fe remains and some Fe,S, is formed -2 A white hot rod of iron is plunged into molten S, the FeS formed flows off, the operation is repeated as long as any S remains (Gahn, Rammelsberg, B B 1862 681) -3 By ppg a ferrous salt by an alkalı sulphide, pre-

ferably NH, sulphide

Properties -FeS prepared in the dry way is yellow-brown, lustrous, metal-like solid, crystallising in hexagonal prisms, S.G. 469 Non magnetic, not changed by heating out of contact with air or in H FeS prepared in the wet way is an amorphous, greenish black powder, which on gently heating in air is partly changed to FeSO,, it is slightly soluble in water By ppg FeS in a very dilute solution, and then dialysing away the other products of the reaction, Winssinger (Bl [2] 49, 452) obtained a very dilute solution of colloidal FeS, the solution was greenish brown, oxidised and coagulated very readily

Reactions -FeS prepared in dry way 1 Heated in hydrogen, or out of contact with air 18 unchanged -2 Heated in steam evolves H and H.S. and leaves a black magnetic mass con taining Fe₈O₄ (Regnault, A Ch [3] 62, 379) -3 Heated strongly in air forms Fe₂O₃ and SO₂-With dilute hydrochloric or sulphuric acid evolves H2S, and forms FeCl2 or FeSO, -5 Ox1 dised by nitric acid -6 Heated with chlorine

from S2Cl, and FeCl,

FeS prepared in the wet way 7 Oxi dises in air at ordinary temperature, forming Fe₂O₂ xH₂O₂ S, and a little basic Fe sulphate (Wagner, D P J 192, 131) -8 Slightly soluble in water, re-ppd by NH, HS -9 Soluble in sulphurous acid solution, also in potassium cyanide solution (Goueront, O R 75, 1276) — 10 Slightly soluble in solutions of alkaline sul phides -11 Very easily decomposed by acids, with evolution of H2S

FEBROSO FERBIC SULPHIDE Fe,S. (Magnetic sulphide of iron) Occurs native as magnetic pyrites in he agonal crystals, SG 451 to 464, the composition may be expressed as xFeS.Fe.S., x is very seldom = 1, generally = 5 and 6 The first product of the action of H2S on strongly

FERROUS SULPHIDE FeS (Iron monosulphide | heated Fe,O, is Fe,S, but this decomposes to FeS (Sidot, C R 66, 1257)

(Sesquisulphide of L'ERRIC SULPHIDE Fe2S, sron) By heating a mixture of powdered FeS and S to redness, or by passing H₂S over Fe₂O₂ at 100° (Berzelius, P 7, 393) A greenishyellow mass, magnetic according to Proust (Scher J 10, 54), non magnetic according to Berzelius (Ic) When heated, gives Fe,S, when moist soon chang s to a mixture of S and Fe₂O₃, decomposed by dilute acids forming ferrous salts, H,S, and H,S xS

Combines with Fe.O, when heated with it. The product of the reaction of HS on Fe,O, at somewhat above 100° is Fe O, 3Fe,S, according to Rammelsberg (P 121, 337) Combines with CuS to form CuS Fe2S3, also with K2S, Na2S, These compounds may be regarded as $Ag_{s}S$ sulphoferrites, they belong to the form M'zFe,S,, and are produced by fusing 1 part Fe filings with 5-6 parts S and 5-6 parts alkaline carbonate. the Ag salt is obtained by adding AgNO, to the K salt suspended in water (v Schneider, P 136, 460, Preis, J pr 107, 10) Fe,S, is said to form a hydrate, Fe,S, 3H,O, a greenish black pp ob tained by adding NH, HSAq to a ferric solution containing an oxidiser such as Cl or a hypochlorite (Phipson, C N 30, 139)

IRON DISULPHIDE FeS, (Iron pyrites) Occurrence -In large quantities, in regular crystals as · ollow pyrites, and in rhombic crys

tals as white pyrites
Formation -1 By slowly heating a mixture of Fe₂O₃, S, and NH,Cl (Wöhler, P 37, 238) -2 By the action of CS₂ on Fe₂O₂ (Schlagden hauffen, J Ph [3] 34, 175) -3 By heating Fe, or Fe,O₃, with SO₂Aq in a sealed tube to 200° (Geitner, A 129, 350) -4 By passing H₂S over an oxide or chloride of Fe at a temperature above 100° but below redness -5 By the action of organic matter on water containing Fe and sulphates in solution —6 Glatzel (B 23, 37) obtained crystals of FeS, by strongly heating FeCl, with P.S.

Preparation -1 An intimate mixture of 2 parts FeS and 1 part S, or of \ part Fe with \\ \frac{1}{4} \ parts S, is heated in a retort to a temperature somewhat under red heat, and the product is treated with dilute HClAq (Berzelius), below 100° the chief product is Fe S, and at red heat Fe,S4 is formed -- 2 By mixing an alkaline per sulphide solution with FeCl₂Aq at 180° or with FeSO₄Aq at 165° (Senarmont, A Ch [3] 30, 129)

Properties - A bulky dark yellow powder, or crystallised in small brass yellow cubes and octa hedra Not magnetic The rhombic form of FeS. oxidises in moist air forming FeSO,, S, and H2SO.

Reactions -1 White iron pyrites, finely-divided yellow pyrites, or FeS, prepared in the wet way, oxidise in aw, forming chiefly FeSO. and at higher temperatures SO, and Fe₁O₂ — 2 Calcined with carbon, gives CS₂ —8 Not acted on by dilute acids, by decomposed by conc hydrochloric acid, giving H₂S and S —

4 Oxtdised by heating with conc nitric acid

Iron, telluride of Produced by reducing fer-

rous tellurite in H (Berzelius)

MMPM

IRON ALUMS

 $K_2[or (NH_4)_2]SO_4.Fe_2(SO_4)_2.24H_2O_7$ ALUMS, vol i. p 148, and SULPHATES. M M P. M.

elements, IRON, NICKYL, COBALT, and MANGAN ESS, are more or less closely connected. Fe, N1, and Co occur in meteorites, some of which also contain minute quantities of Mn. The chief ores of Fe and Mn are oxides, carbonates, and sulphides, of N1 and Co sulphides and arsenides Fe has been known and used for ages, N1, Co, and Mn have been known from about the middle of the eighteenth centur. The name won is probably a form of the Sanserit word ayas (= metal), the names nuckel and cobalt are derived from terms used by miners in the Middle Ages to express false or spurious metals, or minerals from which no useful metals could be obtained, man ganese is sai to be a corruption from mag-

nesta nigra, a name long given to the mineral pyrolusite Compounds of Fe occur in large quantities, widely distributed, compounds of Mn are not so common, "or so widely distributed, and compounds of Ni and Co occur only sparingly Fe, Ni, Co, and Mn are obtained by reducing the oxides with char coal at high temperatures. The metals are all hard, lustrous, fairly malleable and ductile, they crystallise in the regular system, they are more or less magnetic, they are unacted on by dry air, but oxidise slowly in moist air, they decompose steam, and react with acids to form salts. The following table presents some of the characteristic properties of the four metals.—

	MANGANESE	ibon	NICKEL	COBALT			
Atomic weights	55	55 9	58 6	58 8			
	One compound of Mn (MnCl ₂), and two of Fe (FeCl, and FeCl ₃) have been gasified, no Ni or Co compounds have been gasified, specific heats of the four metals have been directly determined. Molecular weights unknown						
Melting points (approx)	1800°-1900°	1600°	1500°	1500°			
Spec gravs (approx)	8	78	8 9	86			
Spec grav (approx)	6-9	72	6.6	68			
Occurrence and Preparation.	Occurs chiefly as MnO ₂ . Obtained by reducing the oxides by C at a high temperature, Also by reducing the chloride or fluoride by Na.	Chiefly as Fe ₂ O ₁ , Fe ₂ O ₄ , and FeCO ₂ . Obtained by reducing Fe ₂ O ₂ by C, or CO, at a high tem perature, also by reducing Fe ₂ O ₃ or Fe ₃ O ₄ in H, and by electrolysis of 1 eSO ₄ Aq	Chiefly as NiAs and NiAsS Ob tained by reducing Ni ₂ O ₂ by Cata high temperature, or by heating in H.	Chiefly as CoAs, and CoAsS Obtained by reducing Co ₂ O ₄ by heating with Corin H.			
Physical pro- perties			Silver white, very tenacious, hard, ductile, malleable, magnetic up to c 250°, crystallises in regular cubes and octahe dra.	Steel grey, lustrous, hard, very ductile at red heat and up wards, somewhat malleable, magnetic, crys talhises in regular cubes and oc tahedra			
Themscal pro perties	Oxidises easily in air, Mn obtained by reducing chloride by Na is said not to tarnish in ordinary air Oxidised by heating in air Decomposes steam, said to decompose	Unchanged in dry air, in moist air forms Fe ₂ O ₂ xH O ₅ , heated in air or O, burns to Fe ₃ O ₄ and Fe ₃ O ₅ Decom- poses steam, form- ing Fe ₃ O ₄ and H Dissolves in dilute	temperature De- composes steam at red heat Dissolves in dilute soids, but	dinaryair; heated in air or O burns to Co ₂ O ₄ Decom poses steam at red heat, decomposes NH ₂ to N and H Dissolves in di- lute acids, but is unacted on by			
Vos. III	= *		·	F			

TABLE—continued

1 ABLE—continued								
	MANGANESE	IBON	NICKEL	COBALT				
	cold water slowly Dissolves in dilute acids, hardly acted on by cold cone H ₂ SO ₄ Combines directly with Cl and Br No simple cyanide of Mn is known, but the acid H ₄ MnCy ₅ and salts derived from it, and also salts of the hypothetical acid H ₂ MnCy ₅ , have been isolated With acids forms two series of salts, MnX ₂ and MnX ₃ , of which the manganous salts (X = Cl, SO ₄ , &c) are the more stable Besides the oxides corresponding to the salts (MnO and Mn ₂ O ₃) other acid acid H ₂ MnO ₄ , and numerous salts of this acid, are known, salts of the hypothetical acid H ₂ MnO ₄ are also numerous Atom of Mn is divalent in the gaseous molecule MnCl ₂ .	sol in cold cone H ₂ SO ₄ , unacted on by cold cone H _N O ₂ , combines directly with Cl, Br, and I, also with C, and probably with H and N No simple cyande is known, but a large number of ferro and ferri cyanides, and also the acids H ₄ FeCy ₈ have been isolated Some ammonic compounds are known Reacts with acids to form two series of salts, FeX ₂ and FeX ₃ , of which the ferric salts (X = Cl, SO ₄ &c) are the more stable Ferrates, M ⁴ ₂ FeO ₄ , are also known, but neither the corresponding acidnor anhydride has been isolated Atom of Fe appears to be divalent and trivalent in gaseous molecules (FeCl ₂ and FeCl ₃), perhaps also tetravalent (Fe ₂ Cl ₄ and Fe ₂ Cl ₆)	cold cone HNO, Coribines directly with Cl, Br, and I. Probably forms a nitride by heating NiOin NH, A Cy2 and many double cyanides are known, but no acids or salts corresponding with ferro, ferri, mangano, and mangani cyanides have been isolated Some ammonio - com pounds are known With acids forms two series of salts, NiX, and NiX, of which the nickel ous salts (X = Cl, SO; &c) are much the more stable No salts in which Ni forms part of the acidic radicle have yet been certainly isolated	cold conc HNO. Combines di rectly with Cl, Combines di rectly with Cl, Br, and I, also probably with C CoCy, is known, also the acids T.CoCy, and H.CoCy, and H.CoCy, and many salts de rived therefrom Very many ammonio - com pounds are known With acids form two series of salts CoX, and CoX, of which the cobaltous salts (Y = Cl, SO, & & c) are much the more stable By the action of molten KOH on CoO a salt is obtained in which Coseema to form part of the negative radicle				

pounds —O xides — MO, M₂O₃, M₂O₃, also MnO₂, MnO₈, Mn₂O₇, Sulphides — MS, M₃S₄, M₂S₄, MS₄, MCl₃, MnCl₄, Salts — MX_2 and MX_3 , $X = NO_3$, $\frac{SO_4}{2}$, $\frac{PO_4}{3}$, &c Salts containing M in the acidic radicle- $N_{2}MO_{4}$, where M = Mn or Fe, also $N_{1}MnO_{4}$ (? NaFeO₄), also $xMOyFe_2O_3$, where M= decidedly positive metal $Acids-HMnO_4$ The oxides MO are basic They react with

acids to form salts MX2 MnO and FeO are readily oxidised by standing in air, FeO very rapidly. NiO and CoO, on the other hand, are obtained by heating the higher oxides in air The oxides M_2O_4 are basic, forming salts MX_4 In the case of Mn only a few salts corresponding to M₂O₂ are known, eg Mn₂(SO₄). In the cases of Ni and Co the salts of M₂O₂ are hardly known, the cudes dissolve in cold cone solds, probably forming salts, but on warming salts of MO are obtained Both Fe₂O₃ and Mn₂O₄ show feebly acidic properties, as they combine with some more basic oxides, eg CaO, BaO, ZnO

General formulæ and character of com | The oxides M3O4 react with acids, for the most part, as compounds of MO with MO, Ye,O,, however, is said to produce a few corresponding salts, eg Fe,Cl, and Fe,(SO,). It is doubtful whether MnO, form any corresponding salts. with acids it usually evolves O, and forms man ganous salts MnX, It combines with several more positive oxides, eg CaO or BrO, to form compounds $xM^{11}OyMnO_2$ MnO, and Mn₂O, are extremely unstable acidic oxides The acid of Mn₂O₇, vis HMnO₄ or H₂Mn₂O₈, is known, and from it a large series of salts has been obtained The acid of MnO, (H,MnO,) has not been isolated, but the manganates Mi MnO, are well known salts Ferrates, M'2FeO4, corresponding to the manganates, are known although neither the acid H₂FeO, nor the annydride FeO, has been isolated

> The sulphides MS are basic, but MnS shows slightly acidic properties MnS forms a com pound with the very positive K₂S (K₂S MnS), CoS, on the other hand, combines with the slightly negative As₂S, (2CoS As₂S,) Fe₂S, forms compounds with Ag₂S, CuS, &c, which may be regarded as sulphoferrites

The haloid compounds MX₂ or .I₂X₄ are generally formed by direct union of the elen'ents, also by dissolving the oxides MO in the haloid acids HX and evaporating. Fe is the only member of the group which certainly forms haloid compounds containing more halogen than MX₂. There are, however, indications of the existence of MnCl₂, and MnCl₄. The haloid compounds which have been gasified are MnCl₂, FeCl₂ and FeCl₃. The eare no indications of the existence of gaseous molecules Mn₂Cl₄, but the V D s of ferrous and ferric chlorides point to the existence of the gaseous molecules FeCl₂ and FeCl₃ at high tempera ures, and Fe₂Cl₄ and Fe₂Cl₄ at lower temperatures

The salt. of the metals of the iron group be long to the series MX_1 and MX_2 , where $X = NO_3$, $\frac{1}{3}SO_3$, $\frac{1}{3}CO_3$, $\frac{1}{3}PO_3$, $\frac{1}{3}CO_3$, $\frac{1}{3}PO_3$, $\frac{1}{3}CO_3$, $\frac{1}{3}PO_3$, $\frac{1}{3}CO_3$, $\frac{1}{3}PO_3$, $\frac{1}{3}CO_3$, $\frac{1}{3}C$

The only member of the series which forms acidic oxides that have been isolated is Mn (v supra) Permanganic acid, HMnO., has also been isolated, but no oxyacid of Fe, Ni, or Co

The iron elements exhibit analogies with several other families of elements. Their relations with the elements of Group III, especially with Al, Ga and In, are shown in the composition of the salts M_{N_a} , in the existence of alums, $eg \in K_{N_a} M_{N_a} M_{N_a}$, where M = Al, Ga, In, Fe, or Mn, also in the existence and dissociation of the gaseous molecules Fe₂Cl₂, Al Cl₃, and Ga,Cl₄. The analogies shown by Ni and Co to the Al family are very slight

The iron family is distantly connected with the halogens. This is shown in the existence of the salts $N^{\dagger}MO_4$, where M=Mn (°1 c), Cl, or I

The relations between the iron family and the chromium family of Group VI are fairly well marked, the MN salts are similar to the CrX, salts, MnO, resembles CrO, in being acidic and forming salts M12MnO, analogous to and isomorphous with the chromates Ferrates, M1, FeO, are also known, a hough neither FeO, nor H.FeO, has been isolated MnO₂ is not unlike CrO₂ in some of its reactions. The sulpho ferrites, e.g. CuFe2S4, resemble the sulpho chromites, eg The relations of Ni and Co to the ZnCr,S Or family are chiefly shown in the formulæ of the nickelous, cobaltous, and chromous salts, MX₂, in the existence of many ammonio cobalt and ammonio-chromium compounds The formation of the cyanogen acid H,MCy, and of salts of H₂MCy₆, where M = Mn, Fe, Co, or Cr, is a point of similarity between Cr and the iron family

The composition of the salts MX, is similar to that of the salts of Group II, so far as properties go these salts most resemble those of the odd series members of Group II, Mg, Zn, and Od, the ammonio-compounds of To also recall

the ammonio-compounds of Hg which is an odd series member of Group II

There are some resemblances between Cu which belongs to Group I and the iron elements, thus the salts MX, resemble in many respects the cupric salts CuX₂, there are many ammonic-copper compounds, numerous double cyanides of Cu exist and some of those are probably derived from a cyanogen and H₂Cu₂Cy₄.

Finally some of the physical properties of the iron family resemble the properties of the two other families of Group VIII, viz Rh, Ru, Pd, and Os, Ir, Pt, this resemblance is carried out in the formulæ of some of the salts, and in the existence, and in some cases the composition and properties, of numerous complex cyanides; these complex cyanides are indicated in the following table—

 $\begin{array}{ll} H \ MC_{3} \ \ and \ salts. \\ M = Mn, Fe, Co, Os, Ru \\ & M = Fe, Co, Ir \\ Salts \ of \ H_{3}MC_{3} \ \ (acid \ not \ isolated) \\ & M = Mn, Rh \end{array}$

The acid H₂PtCy₄ and salts of this acid exist, salts of H₂PdCy₄ are known. It should be noted that Ni does not form nickelo or nickeli cyanides analogous to any of the complex cyanides formulated above, but only ordinary double cyanides.

The position of the iron family of elements in the classification based on the periodic law is somewhat peculiar (v Table on p 204 of vol 11.) Mn is placed in the even series of Group VII, the only other members of this group as yet known are the halogens Fe, Ni, and Co form a division, or family, of Group VIII, the other families of this group are (1) Rh, Ru, Pd, and (2) Os, Ir, Pt The iron family should therefore, strictly, include only he, Ni, and Co, Mn has been included in this family because of its close relations to Fe, but because of its position in Group VII, Mn has also been included in the halogen family (v Halogen elements, vol 11 p 664) Each of the three families which together con stitute Group VIII is separated from the others by many elements, the analogies between these families cannot be very close The iron family is preceded in order of atomic weights by a series of elements, which begins with the very positive element K and ends with the element Or which is both metallic and non metallic, the iron family is succeeded by series 5 which begins with the undoubtedly metallic Cu and ends with the no less undoubted non metal Br The iron family forms one of the turning points in the swing of properties from very positive to very negative, the next similar turning point is marked by the second family of Group VIII, Rh, Ru, Pd, and the third turning point is marked by the last family of Group VIII, Os, Ir, Pt Recent researches show that Co and Ni ire perhaps separable each into two other elements, v NICKEL in this volume In connection with this article v Chromium group of elements, vol 11 p 168, Copper group of elements, vol 11. p 250, Eabths, metals of the, vol 11 p 424, HALOGEN ELEMENTS, vol 11 p 664 NOBLE METALS, in this vol For detailed properties of the members of the iron group v CoBALT, vol ii p 217, IRON, this vol p 51, Manganese and Nickel, MMPM F 2

ISAMIC ACID v ISATIN. ISATANE v ISATYDE ISATIC ACID C.H.NO. 1.6

C.H. (NH.) CO CO.H o Amido phenyl glyoxylic acid Formed, as potassium salt, by boiling isstin with cone KOHAq (Laurent, A Ch [3] 8, 871, Erdmann, J pr 24, 13) Obtained synthetically by reduction of an alkaline solution of onitro-phenyl-glyoxylic acid with ferrous sulphate (Classen a Shadwell, B 12, 353) By decom posing the lead salt with H2S and evaporating at atmospheric temperature in vacuo isatic acid may be obtained as an amorphous white powder, soluble in cold water The acidified solution deposits, after a while, crystals of isatin, which is its anhydride, and the separation may be hastened by warming With acetone in alkaline solution isatic acid forms (Py 3)-methyl quino line (Py 1) carboxylic acid [241°] Its silver salt forms microscopic needles (W Phtzinger, J pr [2] 33, 100, Beyer, J pr [2] 33, 416) Acetophenone gives, in like manner, phenyl-

quinoline carboxylic acid
Salts - KA' faint yellow crystals, which Salts -KA dissolve in conc KOHAq, forming a deep violet red solution, turned yellow on dilution with water Its solution gives a yellow flocculent pp with lead acetate, and, when concentrated, it is also ppd by BaCl₂—BaA'₂ (at 150°) scales.—AgA' beautiful yellow prisms, sol water

Acetyl derivative C.H. (NHAc) CO CO.H [160°] Obtained from acetyl-isatin by dissolving in cold dilute NaOHAq and ppg with dilute H₂SO₄ (Suida, B 11, 586) Needles (from alcohol) Sl sol cold water, m sol alcohol, ether, and benzene Boiling HClAq converts it into isatin Sodium amalgam reduces it to the acetyl derivative of α oxy o amido phenyl acetic acid $C_0H_4(NHAc)$ CH(OH) CO_2H , which forms colourless needles [142°] converted by HI into oxindole

Chloro satic acid CaHaCl(NH2) CO CO.H From chloro isatin by warming with KOHAq (Erdmann, J pr 19, 339, 24, 5, A 33, 129, Laurent, A Ch [3] 3, 378) Not known in the free state, since, when its salts are acidified, chloro-isatin is formed — KA' light yellow flattened needles (from alcohol), v sol water — BaA', aq pale yellow needles —BaA', 3aq bril hant deep yellow lamine -PbA', 2aq brilliant yellow gelatinous pp, which in a few minutes changes to scarlet PbA'₂aq —AgA' light yellow pp, sol boiling water—The cupric salt is ppd as a brownish red powder, which changes to blood red

Di-chloro-isatic acid C_eH₂Cl₂(NH₂) CO CO₂H Formed by dissolving di chloro isatin in hot Separates on addition of HCl as a yellow pp, which, even when exposed over sulphuric acid in vacuo in the cold, splits up into water and di chloro isatin It dissolves in water forming a light yellow solution, which becomes turbid at 60° and deposits di chloro isatin -KA'aq yellow laminæ — BaA', 2aq golden needles — CuA', reddish brown pp changing to greenish yellow and crimson — AgA', small yellowish needles (from hot water)

Bromo-isatio acid C₆H₃Br(NH₂) CO CO₂H Formed by warming bromo isatin with aqueous caustic potash (Gericke, J pr 95, 176, 257) The free acid splits up at once into water and bromo-

ısatin — L.A' easily sol ible cauliflower like crystals - NaA' warty crystals - BaA'₂ 8aq yellow prisms — CuA'₁ 2aq red granular pp — PbA'₂2aq yellow pp, changing to a scarlet crystalline powder —ZnA'22aq brownish pp, changing to red granular powder -AgA' light yellow needles (from hot water)

D1-bromo-1satic acid C,H,Br2(NH,)CO,H From di bromo isatin and hot KOHAq (Erdmann, J pr 19, 360) The free acid is ppd by adding HCl to a cone solution of the K salt as a light yellow powder, soluble in a large quantity of water By desiccation, even at 15° in vacuo, it is decomposed into di bromo isatin and water —

KA'aq pale yellow needles, v sl sol water Ethylether EtA' [105°] I com the silver salt and EtI (Baeyer a. Oekonomides, B 15, 2099) V sol ordinary solvenus At 110° it gives di bromo isatin

Sulpho-isatic acid

C₆H₈(SO₅H)(NH₂) CO CO₂H From isatin sul phonic acid and excess of alkalı (G a A Schlie per, A 120, 12) Only known in its salts, which are converted by mineral acids into isatin sul phonic acid —K,A"aq waxy yellow prisms, v sol water —BaA"3aq long silky lemon yellow needles, v sol boiling water, insol alcohol -PbA" $1\frac{1}{2}$ aq yellow needles, v sol water $-4g_2A''$ $1\frac{1}{2}$ aq pale yellow needles, sl sol water

Isomeride of isatic acid v m Amido-Phrnyl

GLYOXYLIC ACID

p Methyl isatic acid Acetyl derivative C₆H₃(CH₃)(NHAc)CO CO₂H [172°] white needles, soluble in alcohol and hot water. very sparingly in ether, benzene, ligroin, and CS, Formed by the action of cold aqueous al kalıs upon acetyl p methyl pseudo ısatın

Ethyl ether of the acetyl derivative C.H.(CH.)(NHAC)CO CO.Et [79°] White glistening plates, insol water Formed by boiling acetyl p methyl pseudo isatin with dilute

alcohol (Duisberg, B 18, 198)

Amide of the acetyl derivative C_eH₃(CH₃)(NHAc) CO CONH₂ [141°] Formed by the action of alcoholic NH₃ on the acetyl de rivative of methyl ψ isatin (Panaotović, J pr [2] 33, 72) Trimetric prisms (from alcohol), insol water

ISATILIM v ISATIN ISATIMIDE v ISATIN

C_sH_sNO₂ ie C_sH_s< CO OH ISATIN

(stable form) or $C_{\bullet}H_{\bullet} < \stackrel{CO}{NH} > CO$ (transition form Anhydride of isatic acid or pseudo isatin o-Amido phenyl glyoxylic lactim [201°]

Formation -1 Discovered simultaneously by Laurent (A Ch [8] 3, 371) and by Erdmann (J pr 24, 11) as a product of the oxidation of indigo by nitric acid (L) or chromic acid (E) -2 By oxidising amido oxindole with FeCl. nitrous acid, or CuCl₂ (Eaeyer, B 11, 1228) The oxindole may be obtained from phenyl acetic acid by nitration and reduction (Baeyer, B 11, 583), and converted successively into nitroso oxindole and amido oxindole -8 Prepared by boiling o nitro phenyl propiolic soid with alkalis (Baeyer, B 13, 2259) The reaction possibly takes place as follows.

ISATIN 69

$$C_{e}H_{i} < C_{C}C_{CO_{i}H} + 4H_{e}O$$

$$= C_{e}H_{i} < C_{C}C_{CO_{i}H} + CO_{e} + 4H_{e}O$$

$$= C_{e}H_{i} < C_{C}C_{CO_{i}H} + CO_{e} + 3H_{e}O$$

$$= C_{e}H_{i} < C_{C}C_{CO_{i}H} + CO_{e} + 4H_{e}O$$

(Michael, J pr [2] 25, 255) —4 Together with $N_2(C_8H_4 CO_1H)_2$, by dissolving isatogenic ether in aqueous Na_2C_3 (Baeyer, B 15,55) —5 From isa togenic acid by dissolvin. in H_2SO_4 and adding water (Baeyer B 14, 1742) —6 By oxidising carbostyril with alkaline KMnO₄ (Friedlander a Ostermaier, B 14, 1921) —7 By boiling nitroso (γ) oxy carbostyril with cone HClAq (Baeyer a Homolka, B 16, 2217) —8 By heating anthroxanic acid with FeSO₄ and dilute ammonia (Schillinger a Wleugel, B 16, 2224)

Preparation —1 Finely powdered indigo (50g of 65 pc) is made into a thin paste with boiling water, and a dilute solution of CrO, (30 g) is added The liquid is boiled till it begins to froth strongly, and is then filtered hot, when isatin separates on cooling The yield is moderate (9 g) (Sommaruga, A 190, 369) —2 A mixture of indigo (100 pts), boiling water (300 pts), and nitric acid (70 pts of S G 1 35) is boiled for two minutes, diluted with boiling water (2000 pts), boiled for five minutes more and filtered The isatin separates on cooling It may be purified by dissolving in aqueous KOH, adding HCl as long as it forms a black or brown pp, filtering adding more HCl to the clear yellow filtrate, and washing the red pp of isatin (Forrer, B 17,

976, Hofmann, A 53, 11)

Properties — Yellowish - red monoclinic prisms, a bc = 4251 503, B = 85° 18' (Bodewig, Z K 4, 65) Has no odour, but a bitter taste Sl sol cold, m sol boiling, water, forming a reddish yellow solution V e sol alcohol, sl sol ether The alcoholic solution imparts an unpleasant odour to the skin

Reactions —1 It is not attacked by dilute natric acid, but a stronger acid forms into o oxy benzoic acid, while conc HNO, forms oxalic acid —2 Nitrous acid, acting upon isatin sus pended in water, forms nitro-o oxy-benzoic acid (Hofmarn, A 115, 280), while, in presence of alcohol, nitrous acid forms benzoic acid (Baeyer, a Knop, A 140, 4)—3 Chromic acid in presence of acetic acid forms isatoic acid

$$C_eH_e < {}^{CO}_N > 0 \text{ oh } + O = C_eH < {}^{CO}_N \text{ co.H}$$
 On

the other hand, acetyl isatin C_sH_sCO_{NAc}CO, being a derivative of pseudo isatin, yields acetyl o amido benzoic acid C_sH_s(NHAc) CO H on similar treatment (E v, Meyer a J Bellmann, J pr [2] 33, 30)—4 Chlorine and bromine form products of substitution—5 Cold aqueous caustic potash forms a red solution, which on boiling immediately becomes yellow, and then contains potassium isatate If the solution be concentrated by distillation, decomposition suddenly takes place, aniline and hydrogen being

given off -6 Aqueous ammonia forms isamio Alcoholic NH, gives a variety of products, acid called by Laurent imesatin, imasatin, amisatin, isatimide, and isatilim. Ly heating isatin with alcoholic NH, in sealed tubes Sommaruga (A 190, 371) obtained di imido isatin, oxy-di-imidoisatin, and deoxy imido isatin -7 Isatin combines with alkaline bisulphites -8 SO, has no action -9 H2S gives di thio isatyde -10 So dium amalgam reduces it to isatyde C16H12N2O4 and doxindole C₂H,NO₂—11 Ammonium sulphide reduces it to isatyde —12 Zinc and dilute H₂SO₄ form isatyde—13 Zinc-dust and a little dilute HCl form isatyde and dioxindole (Baeyer, B 12, 1309) —14 Zinc-dust added to a cold solution of isatin in HOAc forms a colourless solution (? of isatin hydride) which becomes coloured again on exposure to the air, isatin being reproduced -15 Aqueous HI (S G 14) at 100° forms isatyde At 140° it forms a darkgreen insoluble mass, whence boiling alcohol leaves a dark grey residue, isatochlorin (C₁₂H₁₄N₁O₂, 2), whilst the alcoholic solution, mixed with water, gives a pp, whence ether extracts red isatopurpurin (C₂₂H₂₂N₄O₂?), while white isatone (C₃₂H₂₄N₄O₃?) remains un dissolved (Schutzenberger, Bi [2] 4, 170) — 16 PCl, forms 'isatin chloride' (Baeyer, B 12, 456) -17 Hydroxylamine forms nitroso oxin dole or isatoxim -- 18 Alcoholic KCy has no action -19 A solution of isatin, warmed with phenyl hydrazine, forms a pp of the phenyl hy drazide —20 In presence of H₂SO, or ZnCl₂ isatin forms condensation products, with (2 mols of) toluene, phenol, di methyl aniline, thiophene, &c, by elimination of water (1 mol) Thus, phenol and H_2SO_1 give di oxy-di phenyl oxindole $C_4H_4 < \frac{C(C_6H_4OH)_2}{NHCO}$, toluene gives di tolyloxindole, while di methyl aniline gives tetra methyl di-amido di phenyl oxindole (Baeyer, B 18, 2642) -21 When heated with phenyl cyanate, for three hours at 130°, it forms the anilide of isatin v carboxylic acid, which crystal lises from alcohol in needles [180°-185°] (Gum pert, J pr [2] 31, 120, 32, 283) -22 Phenyl mercaptan, added to a hot alcoholic solution of isatin, forms silky needles of a compound (C6H3NO2)(C6H3SH), insol water, but decomposed by hot benzene into its components (Baumann, B 18, 890) -23 By boiling with m-amido-benzoic acid and alcohol there is formed an acid which is termed isat amido-benzoic acid $C_eH_e < C_NC_eH_eCO_rH > CO_rGO_T$

benzamide gives, in like manner, the corresponding amide [c 280°] (Schiff, A 218, 192)—24 Heating with tolylene diamine forms C₁₃H₁₁N₂ [290°], which is probably a quinoxaline (Hinsberg, A 237, 344)

Metallic derivatives — C_sH₄AgNO₂ obtained by mixing isatin with water at 0°, adding KOH (1 mol) followed immediately by AgNO₂ (1 mol) (Baeyer a Oeconomides, B 15, 2093) Red pp — C_sH₄AgNO₂NH₃ Formed in presence of ammonia (L) — Cu(C_sH₄NO₂NH₃). From cupric acetate and an ammoniacal solution of isatin (Laurent) Brown pp — Potassiumisatin is present in the violet red solution obtained by dissolving isatin in conc KOHAq

Indophenine reaction - A solution of isatin

70 ISATIN.

in cone H.SO., shaken with benzene containing thiophene, is coloured blue, through formation of indophenine $(q \ v_i)$. A similar reaction is given by most derivatives of thiophene

Combinations with bisulphites C_bH_bNO₂KHSO₃2aq Formed by boiling isatin with aqueous KHSO₃ or by saturating a solution of potassium isatate with SO₂ (Laurent) Large, pale yellow tables, v e sol water and boiling alcohol, sl sol cold alcohol Gives with lead sectate a pp of isatin and lead sulphite—C_bH_bNO₂(NH_a)HSO₃ pale yellow tables, sl sol cold water—C_bH_bNO₂(NH_cO₂H₁)HSO₃ (Schiff, 4.144, 49)—C_bH_bNO₂(NH_cPh)HSO₃ Crystals, v. sol water (S)

Acetyl-\psi-ssatanCoH_\circ CO \ NAc \ CO \ [141°]

Prepared by heating isatin (1 pt) with Ac O (2 pts) for 4 hours (Suida, B 11, 584) Yellow needles (from benzene) V sol benzene and alcohol, sl sol cold water Resolved into isatin and acetic acid by boiling with water, or, more readily with HClAq Cold NaOHAq dissolves it, forming CoH_\((NHAc)\) CO CO_\(Na\) and, on warming, isatic acid Chromic acid in HOAc oxidises it to NHAC CoH_\((CO)\)

Benzoyl- ψ -ısatın $C_eH_4 < CO \atop NBz > CO$ From ısatın and BzCl (Schwartz, C R 56, 1050)

Oxem C₈H₈N₂O₂e C₈H₄ C(NOH) Isat oxem Netroso oxendole [c 202°] Formed by passing nitrous acid into a 1 p c aqueous solution of oxindole (Baeyer a Knop, A 140, 34) Formed also by boiling diazo nitroso oxindole chloride with alcohol and HCl (Gabriel a R Meyer, B 14, 2332) Obtained by treating isatin with hydroxylamine (Gabriel, B 16, 518, Baeyer a Comstock, B 16, 1706) Very slender golden needles Decomposed by fusion V sl sol water, sl sol alcohol Dissolves in KOHAq, forming a dark reddish brown solution Not decomposed by boiling aqueous KOH—C₂H₂AgN₂O₂ orange pp, got by adding dilute NH₂ to an alcoholic solution of isatin and AgNO₃ Dries up to a brick red powder

Mono-ethyl-ether of the oxim

C.H. C(NOEt) C(OH) Isato-ethyl oxim

[188°] Fine yellow needles, soluble in caustic al kalis, formed by the action of ethyl iodide on the silver salt of isatoxim By successive treatment with zinc-dust and HOAc and with FeCl. it is converted into isatin

Onverted into isatin Di ethyl-ether of the oxim $C_{\bullet}H_{\bullet} \subset C(NOEt) \longrightarrow C(OEt)$ Ethyl-isato-ethyloxim Crystalline solid, formed by the action of
ethyl iodide on the silver salt of the mono ethylether (Baeyer a Comstock, B 16, 1706)

Oxim of ψ -isatin $C_0H_1 \subset CO \setminus C$ NOH

Isonitroso- ψ indoxyl Formed by the action of nitrous acid on ethyl indoxylic acid $C_0H_1 \subset C(OEt) \setminus C$ OCO₂H Flat yellow needles

Percompages at about 200° Sol alkalis and

Decomposes at about 200° Sol alkalis and reppd by CO₂ With phenol and H₂SO₄ it does not give Liebermann's reaction Reduction with sinc-dust followed by oxidation with Fe₂Cl₆ yields isatin.

Ethyl ether of the oxim of ψ isatim $C_*H_* \subset CO$ (NOEt) From ψ isatoxim, KOH, and Etl yellow plates, dissolves in sodium ethylate with a blue colour, reduction with zinc dust followed by oxidation with Fe/Cle yields isatin Forms a violet solution when warmed with aqueous NaOH

Dr-ethyl-derivative of the oxim of ψ -isatin $C_0H_i \subset CO \setminus C(NOEt)$ [99°], yellow needles, sublimable, easily soluble in alcohol and ether, sparingly in hot water, insol alkalis. On reduction with zine dust and oxidation with Fe,Cl, it yields ethyl-pseudo isatin (Baeyer, B 15, 782, 16, 2191)

Phenyl hydrazide $C_{11}H_{11}N_1O$ [211°] Fine yellowish red needles Foi med as a yellow crystalline pp by boiling a solution of isatin in 1,000 pts of water with phenyl hydrazine hydrochloride $(q \ v)$, the pp is quite distinct with a solution of 1 in 20,000 (E Fischer, B 17,577)

Chloride C₈H₄CINO ie C₈H₄⟨CO⟩ CCl [c 180°] Formed by warming isatin (5g) with PCl₂ (7g) and benzene (9g) (Baeyer, B 11, 1296, 12, 456) Brown needles Decomposed on fusion V sol ether, forming a blue solution Decomposed by moist air Potash converts it into isatin HI gives indigo, zinc dust and HOAc do the same

Chloro-natin C₂H₂ClNO₂ [243°] S 1 at 0°, c 5 at 100° Obtained by passing chlorine in sunlight into boiling water containing isatin in suspension The mono and di chloroisatin are separated by recrystallisation from alcohol, in which the former is much less soluble (Hofmann, A 53, 12, Laurent, A Ch [3] 8, 452, Irdmann, A 33, 129, Dorsch, J pr [2] 33, 49) Orange prisms (from alcohol) V sl sol water and alcohol Its solution imparts an unpleasant odour to the skin Decomposed on fusion Hot KOHAq forms potassium chloro isatate Distillation with NH, gives p chloro annine An am moniacal solution of AgNO₃ added to an alcoholic solution of chloro isatin ppts C₆H₂ClAgNO₂NH,

Di chloro isatin C,H3Cl2NO, [186°] tained from the alcoholic mother liquors that have yielded chloro isatin Small, reddish yellow needles or short laminæ (from alcohol) When thrown upon solid M sol alcohol potash, moistened with alcohol, a red solution is formed which solidifies to a violet black magma of C₈H₂KCl₂NO₃, the solution of which gives a pp with AgNO₃ Hot aqueous KOH forms potassium di chloro isatate Distillation with KOH forms di chloro aniline Chlorine does not act on its aqueous solution, but with its alcoholic solution it forms tetra chloro quinone and other bodies KHSO, forms light yellow needles of C,H,Cl,NO,KHSO,, sl sol boiling water Di chloro isatin (10 g) oxidised by CrO₂ (15 g) in glacial acetic acid (60 g) as described under Bromo isatin toims di chloro

Isatoic acid (q v)
Bromo isatin C,H,BrNO, s c.
CBr CH,C CO

CH CH CN COH [255°] Formed, to gether with di brome isatin, by the action of bromine and water on isatin (Eidmann, J. pr.

ISATIN 71

19, 858, Hofmann, A 53, 40) The product is exhausted with boiling water and the crystals that separate on cooling are recrystallised from alcohol whence bromo-isatin crystallises first Aqueous KOH converts it, Orange prisms even in the cold, into potassium bromo-isatate Distillation with KOH yields p bromo aniline When mixed with alcoholic ammonium sulphide and exposed to the air it yields bromoindigo Bromo isatin (10 g) is oxidised by a mixture of gla ial acetic acid (90 g) and CrO. (15 g) to bromo-isatoic acid The mixture must first be kept ice-cold but after 12 hours it may be slowly raised to 10° The product, when cold, is poured into cold dilute H₂SO₄ and the yellow sandy powder crystallised from a mix ture of alcohol and acetone (Dorsch, J pr [2] 33, 45)

cetyl derivative C.H.BrAcNO. [172°]
Formed by boiling brome isstin (5 pts) with
Ac.O (8 pts) (Baeyer a Oeconomides, B 15,
2096) Long straw-yellow prisms (from benzene)

Chloride C.H.BrClNO Formed by treating bromo isatin with PCI, (Baeyer, B 12, 1315) Reddish brown needles, sol hot benzene and ether HI gives bromo-indigo

Oxim C₈H₄BrNO(NOH) From isatoxim and bromine water in the cold (Baeyer a Knop, A 140, 35) Crystals, sl sol wat r

Di bromo isatin | | | CBr CH C CO CBr CH C N

[250°] Formed as above or by digesting bromo isatin or isatin with bromine in sunshine Formed also by heating bromo isatin (1 mol) with bromine (2 mols) in HOAc for 20 hours (Baeyer a Oeconomides, B 15, 2098) Orange prisms (from alcohol) Gives di bromo aniline when distilled with KOH —C₄H₂Br KNO₂ bluish violet scales, sl sol water Very stable but converted into di bromo isatate by warming with KOHAq -AgA' brownish violet powder -C,H,Br,NO,KHŠO, yellow solid, v sl sol water

Oxim C₈H₄Br₂O₄N₂ or C(NOH) C(OH) Formed by the

action of hydroxylamine on di bromo isatin (Baeyer a Comstock, B 16, 1708) Yellow pointed needles Carbonises without melting at about 255° Sol caustic alkalis but precipitated by CO₂

Mono-ethyl-ether of the oxim

O₆H₂Br₂ C(NOEt) N C(OH) Di-bromo isatoethyl oxim. [252°] Yellow needles, formed by the action of ethyl iodide on the silver salt of di bromo isatoxim

Diethyl ether of the oxim

C.H.2Br.2 C(NOEt) C(OEt) Diebromo ethylisato ethyl oxim [116°] Long yellow, silky needles, formed by the action of ethyliodide on the silver salt of the mono ethyl ether

Tri brome isatin Ox*m $C_8HBr_2 < C(NOH) > [162°]$ From the exim of isatin and bromine in excess (B a K) Dirty violet needles (from alcohol) Insol

water, v sol boiling alcohol. At 190° it sublimes as red needles

Mitro isatin C_sH_sNO_s(NO_s) [226°-230°] Prepared by nitration of isatir dissolved in H_sSO_s by addition of powdered KNO_s (Baeyer, B 12, 1312) Sparingly soluble in water, more easily in alcohol

Bromo nitro isatin

C₆H₂(NO₂)Br<CON COH [237°] From bromosatin, KNO₂ and H₂SO₄ (Dorsch) Clumps of orange crystals (from alcohol) Sol acetone, glacial acetic acid and alcohol, al sol benzene and chloroform, v sl sol water and ether Forms a dark red solution in NaOH,Aq, whence an orange powder presently separates

ALKYL DERIVATIVES
Alkyl derivatives of isatin are either derived from the stable form $C_4H_4 < {}^{CO}_N > C$ OH

or from the transition form $C_eH_e < \stackrel{CO}{NH} > CO$ (pseudo isatin) Alkyl iodides acting on silverisatin form alkyl derivatives of stable isatin $C_eH_e < \stackrel{CO}{N} > C$ OR

Alkyl derivatives of pseudo-isatin C_cH_s, CO_{NR} CO are formed by the action of an alkaline solution of bromine or chlorine followed by alcoholic NaOH on the methyl-, ethyl, phenyl, &c indole carboxylic acids which are obtained by the action of HCl on phenyl methylhydrazine pyruvic acid, cc (Fischer a Hess, B 17, 559)

Methyl derivative of isatin C₂H_sO₂N(CH₂)

Methyl-isatoid C₁,H₁₂N₂O₄(?) [219°] Formed by spontaneous change by keeping methyl isatin (Baeyer a Oeconomides, B 15, 2094) Small yellow needles, sparingly soluble in all solvents Dissolves in dilute NaOH on boiling, and on adding acid isatin is precipitated

Methyl derivative of brome-isatin C₂H₂BrO NMe [147°] Formed by the action of MeI on the silver compound of brome-isatin (Baeyer a Oeconomides, B 15, 2095) Red needles

Bromo-methyl-isatoid [231°] Formed by spontaneous change of methyl bromo-isatin by keeping (B a O)

Methyl-pseudo-isatin C,H,NO, i.e C,H,
CO (134°) Red needles

Formation —1 By the action of a cold alkaline solution of bromine or phlorine followed by hot alcoholic NaOH on methyl indole-carboxylic acid [212°], which is obtained by heating phenyl methyl hydrazine pyruvic acid with HOl (Fischer a Hess, B 17, 563)—2 By boiling di-

78 ISATIN

bromo-methyl oxindole with water (Colman, O J 55, 5, A 248, 118)

Reactions — Dissolves in alkalis with a yellow colour With H₂SO, and benzene containing thiophene it gives the indephenine reaction Gives a crystalline compound with phenyl-hydrazine Yields the same product on oxidation in alkaline solutions as in acid solution, viz methyl-di-oxindole

Oxim $C_eH_4 < C(NOH) > CO$ [180°-183°] From methyl-pseudo isatin and hydroxylamine sulphate in hot aqueous solution (Colman, CJ55, 6) Tufts of small pale yellow needles, m sol. hot water, sl sol cold water, v sol alcohol, acetone, ether, and benzene

[146°] Formed by the action of phenyl-hydrazine hydrochloride and NaOAc on an aqueous solution of methyl wisatin A less pure product is produced by the action of phenyl hydrazine hydrochloride on dibromomethyloxin dole (Colman) Fascicular group of small yellow needles, insol water and petroleum ether, sl sol. ether, v sol hot alcohol or benzene

p-Methyl-isatin C,H,NO, te

$$C_oH_oMe < CO \atop N$$
 COH (stable form) or $C_oH_oMe < CO \atop NH > CO$ (transition form)

Tolisatin Anhydride of amido tolyl-glyoxylic acid [184°] (P), [187°] (M)

Formation — From p toluidine and di chloroacetic acid by digestion in alcoholic solution, the resulting p toluide (p-tolyl methyl imesatin) C=NC_cH₄Me

Co.H.Me CO being decomposed by

HCl, and the crude product purified by boiling with aqueous KOH, ppg with HCl, and crystal lising from alcohol and afterwards from water (P J Meyer, B 16, 2261, Fr Baeyer a Co, B Ref. 17, 367, Panaotović, J pr [2] 33, 57)

Properties—Red crystals or glistening red

Properties—Red crystals or glistening red plates Sol hot water and alcohol, sl sol cold water, v sol hot HClAq Dissolves in cold alkalis with a deep-violet colour, and on heating or standing it then takes up water, becoming yellow and forming methyl isatic acid Dissolves in cone H₂SO₄ with a red colour Gives the in dophenine reaction CrO₃ in acetic acid forms methyl isation acid Boiling with Ac₂O for three hours forms the acetyl derivative of methyl-ψ-isatin

Acetyl derivative of methyl- ψ isatin C_eH₂Me CO NAc CO [172°] Formed by boiling p-methyl- ψ isatin with Ac₂O for 3 hours (Panaotović, J pr [2] 33, 71) Formed also by the action of HCl upon the acetyl derivative of p-methyl- ψ -isatin p toluide (Duisberg, B 18, 197) Lemon-yellow needles (from benzene), sol chloroform and benzene, sl sol water, alcohol, ether, ligroin, and CS₂. Converted by cold dilute alkalis into acetyl-p-methyl-isatic acia Alcoholic NH₂ converts it into the amide of acetyl-p-methyl-isatic acid C₂H₂Me(NHAc) CO CONH₂, which crystallises from alcohol in trimetric columns [141°] CrO₂

in HOAe exidese it to methyl esatore seed, which crystallises from boiling sloohol in trimetric plates and, when heated, decomposes at 245° with great increase in bulk, finally melting at 800°

 $Oxim C_iH_iMe < C(NOH) > Isomtroso$ methyl oximole [226°] Formed by the action of hydroxylamine (base' on p methyl isatin (P J Meyer, B 16, 2268, Long yellow prisms, sol alcohol and NaOH, sl sol weter

Phenyl hydraside of methyl isatin $C_sH_sMe < C_s(N_sHPh) > COH$ From p methyl isatin and phenyl hydrazine (P) Golden needles (from chloroform) Nearly insol water, sol al cohol May be sublimed at 240°, but melts above 300° with evolution of gas

Disphenyl-hydraside of methyl visatin C.H.Me (N.HPh) C(N.HPh) [255°]

Formed by warming the acetyl derivative of methyl-visatin with phenyl-hydrazine (P) Yellow trimetric columns (from alcohel) decomposed by fusion Nearly insol water, sol chioro

form $Imide\ C_bH_sN_2O\ or\ C_{1e}H_{1e}N_4O, \quad p\ Methyl$ $imsatin\ Formed\ by\ heating\ p\ methyl\ isatin\ p\ tolunde\ with\ alcoholic\ NH,\ at <math>100^\circ\ (P\ J\ Meyer,\ B\ 16,\ 2264)$ Nearly colourless fine silky needles V al sol hot alcohol and hot water Insol cold alcohol and water Is not re converted into p\ methyl\ isatin\ by\ acids or\ alkalis

Phenyl imide C18H12N2O 1e

 $C_sH_s(CH_s) \subset C(NPh) \supset COH$ Methyl - ssatun anilide Phenyl - methyl imesatin [240°] Formed by heating p methyl isatin with an absolute alcoholic solution of aniline (Meyer, B 16, 2267) Thick yellowish red tables or prisms Sol hot alcohol, al sol cold alcohol and water Heated with acids or caustic alkalis it is resolved into its constituents

o Tolyl ımıde C₁₆H₁₄N₂O s.s

C₆H₃(CH₃) $\stackrel{\frown}{\sim}$ C(NC,H₃) $\stackrel{\frown}{\sim}$ C OH o Tolude of methyl-ısatın o-Tolyl p-methyl imesatın [191°] Red prismatic crystals Formed by heating p-methyl isatın with an absolute alcoholic solution of o toluidine By HCl or hot NaOH it is resolved into its constituents (Meyer, B 16, 2268)

p-Tolyl-smide $C_{1e}H_{1i}N_2O$ s.e $C_{e}H_{4i}(CH_{2i}) < C(NC_{e}H_{2i}) > C$ OH p Tolunde of methyl satin p Tolyl p-methyl smesatin [259°] Formed by heating di chloro acetic acid (1 mol) with p tolundine (4 mols) at 100° C, either alone or in aqueous or alcoholic solution, the yield is 70 pc p Tolyl amido p

tion, the yield is 70 p c p Tolyl amido p

methyl-oxindole C₆H₂Me

CO

is

CH

NH(C,H₂)

first formed and then undergoes oxidation by

absorption of oxygen from the air Formed also by heating dichloracetamide (1 mol) with p toluidine (8 mols), and by heating p methylisatin with an absolute alcoholic solution of p-toluidine (Meyer, B 16, 2261) Glistening yellow needles or plates Sol ether and hot alcohol, sparingly sol cold alcohol, insol water By cold

HCl it is resolved mto p toluidine and p methylisatin Hot HCl or hot NaOH gives p methylisatic acid—Sodium salt crystallises in red prisms, decomposed by water

Acetyl derivative

C.H.Me CO [122°] Glistening red

needles, insol water By HCl it is split up into p toluidine and the acetyl derivative of pmethyl pseudo isatin (Duisberg, B 18, 190)

Bromo p toluide C₁₈H₁₁BrN₂O [210°] Red needles or prismr By heating with ands or alkalis it is split up into its constituents (P J Meyer, B 16, 2267)

 ν o D methyl ψ -isatın \cup_{\bullet} H₃Me<CONMe>CO

Methyl \$\psi\$-o tolisatin [157°] Formed by adding pyruvic acid to a solution of methyl-o tolyl hydrazine in dilute HCl, and warming the resulting oil with a large quantity of phosphoric acid (S G 1 17) The resulting di methyl indole carboxylic acid is then warmed with NaOCl in slightly alkaline solution, when a product [152°] is obtained, which when warmed with water yields the di methyl isatin (Hegel, \$A\$ 232, 221) Brick red needles (from water)

rp D1 methyl ψ isatin C_cH₁Me CO NMe CO [148°] Formed in like manner from methyl p tolyl hydrazine and pyruvic acid, the di methyl indole carboxylic acid giving with alka line hypochlorite a chlorinated compound crystallising in yellow needles [135°] which yield the di methyl isatin on dissolving in water (H) Red needles

Ethyl pseudo isatın $C_0H_4 < \stackrel{CO}{NEt} > CO$ Lac-

Formation -1 By the action of a cold alka

tam of ethyl isatic acid [95°]

line solution of chlorine followed by hot alco holic NaOH on ethyl indole carboxylic acid [183°] which is obtained by the action of HCl on phenyl ethyl hydrazine pyruvic acid (E Fischer a Hess, B 17, 566)—2 By reduction of the di ethyl derivative of pseudo isatin-w-oxim C_eH₄ CO C(NOEt) with zinc-dust and oxidation of the product with Fe₂Cl₄ (Baeyer, B 16, 2193) Large red plates, sol hot water, alcohol and ether With thiophene and H₂SO₄ it gives a blue colouring matter soluble in ether It dissolves in alkalis with a yellow colour, at once forming a salt of ethyl isatic acid C_eH₄ CO CO₂H NHEt

Ethyl pseudo isatin a-oxim

C.H. C(NOH) CO [162°] Yellow four-sided prisms Formed by the action of hydroxyl amine on ethyl pseudo-isatin On reduction with zinc dust followed by oxidation with Fe₂Cl₂ it yields ethyl pseudo isatin It does not yield indigo on treatment with ammonium sulphide (Baeyer, B 16, 2196)

Ethyl pseudo-isatin w-oxim Ethyl ether C₄H₄ CO C(NOEt) [99°] From the ethyl ether of the w-oxim of \(\psi \)-isatin by further ethylation (Baeyer, B 16, 2191) Yellow needles. v.

sol alcohol and ether, sl sol hot water May be sublimed Insol alkalis After reduction with zinc dust, on oxidation with FeCl, it yields ethyl \(\psi\) isatin

Bromo-ethyl-isatin C.H.BrO.NEt s.c.

 $C_*H_*Br < {}^{CO}_N > COEt$ [109°] From the silver compound of bromo isatin and Eti (Baeyer a Oeconomides, B 15, 2095) Long red prismatic needles (from benzene) On keeping it slowly changes into bromo ethyl isatoid

Bromo-ethyl isatoid C₁₈H₁₂Br₂N₂O₄ [245°] Fine needles Sparingly soluble in all solvents, most easily in hot alcohol and acetone Formed by spontaneous change of ethyl bromo isatin by keeping, also by the action of acetic anhydride on ethyl bromo isatin (Baeyera Oeconomides, B 15, 2095)

p Ethyl-isatin C10H2NO2 s.e

C_sH_sEt $\stackrel{CO}{N}$ C OH [137°] Long red needles (Paucksch, B 17, 2805) Formed by heating with HClAq the product of the action of dichloro acetic acid on p-amido phenyl-ethane C_eH_sEt(NH_s) [14]

Di-bromo-ethyl-isatin C₂H₂O₂NBr₂Et : e

 $C_sH_2Br_2 < {C_N \choose N} > C$ OEt [89°] From silver dibromo isatin and EtI (B a O) Red crystals p Methyl ν ethyl- ψ isatin

C_sH_sMe CNLt CO [110°] Ethyl \(\psi -p\)-tolusatin Formed from the p-toluide by treatment with cone HClAq (Duisberg, B 18, 197) Formed also from methyl ethyl indole carboxylic acid by treatment with a weak alkaline solution of NaOCl, and warming the resulting pp with water (Hegel, A 232, 219) Red needles or prisms, v sol alcohol, ether, benzene, and CS, sl sol water and ligroin Sol aqueous alkalis. Gives the indophenine reaction

p-Tolylimide C_eH₃Me C(NC_eH₄Me) CO

p Toluide [152°] Formed by boiling the p tolylimide of p methyl isatin with NaOEt and EtBr (Duisberg, B 18, 198) Large orange-red prisms, v sol alcohol, acetic acid, benzene, and CS_n, al sol ether, insol water Split up by HCl into p toluidine and methyl ethyl-\psi isatin

Isobutyl-bromo-isatin

 $C_{\bullet}H_{\bullet}Br < \stackrel{CO}{N} > COC_{\bullet}H_{\bullet}$ Crystallises with difficulty Is converted by $Ac_{2}O$ into iso butylbromo isatoid $C_{20}H_{10}Br_{2}O_{\bullet}$ [210°] which crystallises in slender needles, sl sol all solvents (Baeyer a Oeconomides, B 15, 2097)

Bensyl \$\psi\$-isatin \$C_sH_s\$\bigce\frac{CO}{N(CH_ph)}\$\bigce\$ [131°]. Formed by adding a solution of sodium benzyl indole carboxylate to one of NaOCl The pp is dissolved in alcoholic NaOH, warmed gently, diluted with water, freed from alcohol by distillation, and ppd with water (Antrick, \$A_227, 364) Long silky red needles (from water) \$A most insol cold water, \$v\$ sol alcohol and ether

Phenol-1satin v DI OXY-DI PHENYL-OXINDOLE.
Tolu-isatin v DI TOLYL-OXINDOLE

(a)-Maphth-isatin C.H. COO or

C₁₀H₀<0 OH [255°] Formed by dissolving (a) naphthoxindole in alcohol and adding HOAc and NaNO. The isonitroso derivative so obtained is reduced with Sn and HCl, and subsequently oxidised with Fe₂Cl_e (Hinsberg B 21, 117) Red needles Forms a compound with phenyl hydrazine [270°]

(β)-Naphth-isatin $C_{10}H_6 < N_{CO} > COH$ [248°]

Formed by dissolving (3) naphthoxindole in HOAc and adding sodium nitrite The isonitrosobody formed yields on reduction with Sn and HCl, and subsequent oxidation with Fe₂Cl₆, the isatin (Hinsberg, B 21, 115) Red needles, v sol ordinary solvents

AMMONIACAL DERIVATIVES OF ISATIN

Imesatin $C_8H_8N_2O$ to $C_6H_4{\stackrel{CO}{<}}C_N>C$ NH_2 or

 $C_eH_4 < CO > C NH$ (?) or $C_eH_4 < C(NH) > C OH$

Isatin imide (?) Obtained by Laurent (J pr 25 457) by passing dry NH, into a boiling alco holic solution of isatin containing a little isatin in suspension Could not be obtained by Sommaruga (B 10, 432) Rectangular prisms insol water, v sl sol ether, m sol boiling alcohol Readily decomposed by heating with alcohol and HClAq into isatin and NH, KOH acts in like manner

Chloro-imesatin C.H.CINO From chloroisatin and alcoholic NH_3 (Laurent) Yellow six-sided prismatic tables, v sl sol boiling alco hol, insol ether Dissolves in KOH, giving a red liquid

Brome-imesatin C₈H₅BrN₂O From brome-isatin and boiling alcoholic NH₃ (Gericke, Z **1865**, 593) Yellowish brown crystalline mass

Iso-amyl-imesatin $C_8H_5(C_5H_{11})N_2O$ is

 $C_6H_4 < \stackrel{CO}{N} \subset NHC_5H_{11}$ or $C_6H_6 < \stackrel{C(NC_3H_{11})}{N} \supset COH(?)$ Formed by heat ing isatin with isoamylamine (Schiff, A 144, 53, Z [2] 4, 13) Yellow lamine, sl sol ether, v sol alcohol Decomposed by dilute acids or by prolonged treatment with water into isatin and isoamylamine

Phenyl-mesatin C₈H₅(C₆H₅)N₂O Anrlide From isatin and aniline in boiling alcoholic solution (Engelhardt, J 1855, 541) Formed also by heating the compound of isatin with bisulphite of aniline, and crystallising from ether alcohol

Chloro - phenyl - imesatin $C_8H_5(C_9H_4Cl)N_2O$ From isatin and chloro aniline (E) Yellowish crystals

Bromo-phenyl-imesatin C₈H₅(C₆H₄Br)N₂O Resembles the preceding (E)

Phenyl - chloro - imesatin C₄H₄Cl(C₅H₅)N₂O Formed by adding aniline to a boiling solution of chloro isatin in alcohol (Engelhardt, J pr 65, 260) Yellow needles, insol water, v sol lot alcohol Resolved by boiling dilute acids into chloro-isatin and aniline Potash gives aniline and potassium chloro-isatate.

Phenyl-bromo imesatin C.H.Br(C.H.)N.O Resembles the above (E)

Di-phenyl-di-ethyl-di-amide isatin C.H. CONPhEt), or CaHan,NO

C.H. C(NPhEt)2>COH(?) So-called phenyl From isatin by heating with ethyl ı**m**esatın ethyl aniline (Schiff) Yellow laminæ, sl. sol. ether, v. sol. alkalis. Split up by acids, alkalis, or hot water into isatin and ethyl aniline

p-Methyl-imesatin v Imide of p Methyl

ısatın (supra)

Phenyl-p-methyl-imesatin v. Anilide of p-

multhyl isatin (supra)
Imasatin C₁₆H₁₁N₂O₃ Formed by passing NH, into a boiling saturated solution of isatin in dilute alcohol (Jaurent, A Ch [3] 3, 483) Greyish yellow granules, insol water and ether, v sl sol boiling alcohol Not attacked by boil ing aqueous HCl Caustic potash dissol es it, and the solution is ppd by dilute HClAq

Di-chloro-imasatin C18H2Cl2N3O2 chloro satin and alcoholic NH, (L) Slightly

reddish powder

D1-bromo-imasatin C14H,Br2N,C3 Formed by heating an alcoholic solution of bromo isatin with ammonia (Gericke, Z 1865, 593) Brownish yellow crystalline granules

Tetra-bromo-imasatin C_{1s}H₁Br₄N₅O, From tetra bromo isatin and alcoholic NH₄ Reddish From

yellow scale. (L)

Amasatin C₁₆H₁₄N₄O₃ Isamıde Amide of Isamic acid? One of the products of the action of ammonia on isatin Prepared by heating ammonium isamate till water is given off, and washing the residue with water (Laurent, A Ch [3] 3, 488, J pr 35, 117) Yellow powder, insol water, nearly insol ether, v sl sol alcohol, m sol boiling alcoholic NH₃ Cold KOHAq dissolves it, giving off NH₃, and forming a yellow liquid containing potassium isamate HClAq forms a violet solution containing isamic acid

Di-chloro-amasatın C₁₆H₁₂Cl N₄O₃ powder, formed by evaporating a solution of

ammonium chloro isatate (L)

Tetra - chloro - amasatın JIGHIOCLNIO. Formed by heating ammonium di chloro isatate

Di bromo amasatin C₁₈H₁₀Br₂N₄O₃(?) Formed by evaporating an aqueous solution of ammonium bromo isatate and treating the pasty residue with water (Gericke) Orange vellow substance, sl sol water, insol alcohol and ether Dissolves with violet colour in acids

Amisatin $C_{18}H_{39}N_{11}O_9$. A product of the action of dilute alcoholic ammonia on isatin and ppd by adding water to the solution after isatimide and isatilim have crystallised out (L) Minute needles, insol alcohol, sol alcoholic

potash

Isamic acid C16H13N3O4 Produced by the action of warm ammonia on isatin, but is best prepared by dissolving isatin to saturation in aqueous KOH, evaporating the solution to dryness, dissolving in alcohol, adding a very concentrated solution of ammonium sulphate, fil-The resi tering, and evaporating to dryness due contains amasatin and ammonium isamate, and the latter may be dissolved in alcohol, whence, after addition of HCl, isamic acid crys tallises (Laurent, A Ch [8] 8, 490) Ruby coloured hexagonal tables or scarlet trimetric lamins. Sl. sol. boiling water, forming a yel

low solution, v sol hot alcohol, m sol ether silvery scales -CieH10KN3O, 12aq silvery plates Aqueous HCl dissolves it with violet colour, and it separates again from the solution in violet crystals turned red by water Boiling dilute acids split it up into isatin and ammonia mine forms 'indelibrome,' a yellow substance

C_{1e}H_sBr₄N₂O₃ insol water Salts - NH₄A' small needles, or very acute minute rhombs When strongly heated it gives off water and forms amasatin Its solution does not ppt salts of ba, Ca, or Mg, but gives a yel low pp with lead acetate and with AgNO, and a red pp with HgCl₂.—The potassium salt may be boiled without decomposing -AgA'

Di chloro is mic acid CieHiiCl2N2O4 Formed by adding HCl to a solution of di chloro ama satin in dilute KCH and crystallising the brick red pp from alcohol (L) Bright red elongated hexagonal laminæ More sol alcohol and ether than isamic acid Forms yellow solutions Decomposed by distillation HClAq forms a violet solution, but on boiling it is split up into NH, and chloro isatin

Tetra chloro isamic acid CieH,Cl,N,O, boiling tetra chloro amasatin with alcohol and adding silver nitrate a flocculent precipitate of

C14H8AgCl4N3O4 is formed (L)

Di bromo isamic acid C₁₆H₁₁Br₂V₃O₄ Formed by dissolving di bromo amasatin in KOHAq and neutralising with dilute HCl (Gericke) Red powder, nearly insol water, v sol alcohol and ether HClAq gives a violet solution Boiling KOHAq gives brome isatic acid —KA' yellow needles, si sol water —BaA'₂
Isatimide C₂₄H₁₇N₅O₄ Formed by passing

dry NH, over isatin moistened with alcohol When absolute alcohol is (86 to 100 pc) used, imasatin first crystallises out, and the filtrate deposits isatimide as a yellow crystal line powder Insol water, scarcely sol boiling alcohol or ether, v sol boiling alcoholic NH, Potash dissolves it with yellow colour and evolution of NH3, the liquid then containing isatin

Isatılım C, H₁₆N₄O₅ (?) Sometimes formed when dry NH3 is passed over isatin moistened with alcohol, separating from the alcoholic fil trate from which isatimide has separated (Laurent, J pr 35, 121) Yellow amorphous flocks, easily decomposed by KOH

Di isatin diamide C1. Hi. N.O2. Formed by saturating an alcoholic solution of isatin with dry NH, and heating to 100° for 24 hours product is filtered boiling, the filtrate contain ing deoxy imido isatin, while the di isatin di amide and oxydiamidoisatin diamide which re main on the filter are separated by treatment with water in which the di isatin diamide is the less soluble (E von Sommaruga A 190, 867, B 11, 1082, 12, 980) Pale yellow crys tals, al sol alcohol and water Nitrous acid forms some di isstin amide

Salts - B'HCl yellow crystalline powder, almost insol cold water --B'HNO, yellow needles --B'H₂SO₄ yellow needles Not de composed by heating with water at 100° --

B'H,CrO, orange powder

Di isatin amide C₁H₁₁N₂O₂ [252°] Formed by warming di isatin diamide with dilute KOH and ppg with HCl (Sommaruga, M 1, 579) Small yellowish needles (from alcohol) Scarcely sol. water, v. sol alcohol —C₁₀H₁₀(NH₄)N₂O₂.

or needles

Dihydride C16H13N2O, [213°] Formed by treating di isatin amide or di ie tin diamide with sodium amalgam (Sommaruga, A 194, 88) Slender needles (from alcohol), scarcely sol water and other Oxidised by boiling with HgO or aqueous FeCl, to di isatin amide Not affected by aque ous KOH (S G 1 27) at 100° -NaC, H, N,O, long colourless needles, v sol hot water -KC1. H12N,O, broad needles with silky lustre

Oxy diamido di isatin diamide C₁₆H₁₄N₆O₃ Oxydiimidodiamidoisatin [295°-300°] Formed as above (S) Large colourless needles water, v è sol alcohol Dissolves readily in acids, and is not reppd from these solutions by NH, Boiling with water and sodium amalgam converts it into di amido di hydrindic acid The solutions of its salts show intense red fluorescence -B'HNO, granules, v sol hot water -B'H.SO, prisms

Di amido di hydrindio acıd C16H16N4O2. [217°] Formed as above Crystalline granules Decomposed on fusion V sol hot water. Oxidised by chromic acid mixture to 'di imidodi hydrindin dicarboxylic acid C1.H12N4O4 which crystallises from hot water in needles

[210°] Deoxyimido diisatin C₁₆H₁₁N₂O₂ Formed as mentioned under dissatin diamide (S), and purified by solution in aqueous KOH and ppn by an acid. Yellowish powder Decomposed by fusion V sol alcohol, hot water,

Oxy amido hydro-isatin, so called, CisH13N3O30 Formed by treating the preceding body with sodium amalgam or by heating it with KOHAq in sealed tubes at 100° (S) Yellowish amorphous powder, insol water, v sol alcohol. Decomposes at 188° without fusion

ISATIN CARBOXYLIC ACID C_{1.}H₁₀N₁O₂ te C₈H₄NO CONPhH, probably CO

C'H' V CONH by Carbanılıdo ısatın

Formed by heating isatin for 3 hours at 130° with phenyl cyanate (Gumpert, J pr [2] 32, 283) Crystallises from benzene in canary yellow needles Sol alcohol, ether, and glacial acetic acid

Reactions -1 When fused it forms isatin

and phenyl cyanate (compare the formation of isatin from acetyl isatin) -2 With H2SO, and crude benzene it gives the indophenin reaction Dissolves in warm dilute kOH forming potassic carbanilo isatate HCl throws down sparingly soluble carbanilido isatic acid, NPhH CO NH C.H. CO CO.H. [170°-180°, with decomposition] The acid is very stable, but by heating at 110° for a long time it loses H.O. changing back to carbanilido isatin Carbanilido isatic acid, when heated with ethyl or methyl alcohol, splits off CO2 and H2O forming $C_{16}H_{16}N_2O_2$ [175°], and $C_{15}H_{14}N_2O_2$ [197°], respectively – 4 Converted by amines into am des of carbanilido-isatic acid, thus alcoholic NH. at 0100° forms NPhH CO NH CaH, CO CO NH, [229°], orystallising from alcol.31 in needles. It dissolves in dilute NaOH, but is reppd unaltered by HCl When dissolved in glacial acetic acid it is converted by N₂O, into an indifferent body, C₁₄H₁₂N₂O₂, [270°] —5. NEtH₃ forms NPhH CO NH C.H. CO CO NEtH [210°] It forms needles (from alcohol) and is a Phenyl hydrazine forms weak acid -- 6 NPhH CO NH C, H, CO CON(NH2)Ph [193°] -Hydroxylamine forms

NPhH CO NH C.H. CO CO NH OH [225°] ISATIN DIHYDRIDE v DIOXINDOLE

ISATIN INDOGENIDE v Indigo IBATIN SULPHONIC ACID C.H.NSO, .e

 40° H 6° H 6° H 6° O OH Isatosulphuric acid

Preparation —Commercial indigo carmine (18 pts) is stirred up into a thin paste with water (18 pts), H2SO4 (11 pts) is added, and the mixture heated to boiling while K₂Cr₂O₂ (1 pt) is gradually thrown in, as long as decolourisation ensues The hot solution is filtered and KNO₂ added, which facilitates the deposition of potassium isatin sulphonate The K salt is mixed with resinous matter, which can be got rid of by dissolving in hot baryta water, ppg excess of baryta by CO₂, and then ppg by K.SO₄ (G a A Schlieper, A 120, 1) Yellow radio crystalline mass (containing 2aq) Insol ether and benzene, m sol alcohol, v sol water Powerful acid, separating HCl from its salts Not decomposed by H₂SO₄ or HNO₂, even on boiling Aqua regia slowly forms tetra-chloro quinone Alcoholic NH, forms dark brown bodies Hydric iodide does not reduce it Ammonium sulphide forms SO, H C, H, CH(OH) > COH Hot potash forms

sulpho isatic acid Salts - NaA' 2aq Salts — NaA' 2aq deep-red tables, ppd from its aqueous solution by NaCl — KA' aq small golden needles S 5 in the cold Insol alcohol Ppd by KNO, from its aqueous solu water, sl sol NH₁Cl—BaA'₂4aq scarlet powder, usol alcohol, sl sol water—CaA'₂2aq small golden needles, m sol water—AgA' aq. yellow needles, sl sol water

DIISATOGEN C₁₆H₈N₂O₄ 1.6 Q—Q Q—Q

 $C_{\bullet}H_{4} < N = N > C_{\bullet}H_{4}$ (Michael, J pr [2] Prepared by the action of fuming H.SO, on di-o-nitro di-phenyl-diacetylene (Baeyer, B 15, 52) Red needles Sol nitro benzene, sl sol chloroform, insol alcohol and ether With H2SO, and FeSO, it gives indoin It is very readily reduced to indigo by cold NH, HS, by zinc-dust, and NH, NaOH or AcOH, by glucose, and alkalis, &c It combines with ammonium bisulphite ISATOGENIC ETHER C.H.O.N CO.Et to.

or (CO₂Et CO CO C₆H₄)₂N₂ (Michael, J pr [2] 85, 255) [115°] Formed by an isomeric change from o nitro phenyl-propiolic ether by the action of cold H₂SO, (Baeyer, B 14, 1741, 15, 780) Yellow needles By most reducing agents it is reduced to indoxylic ether, but ferrous salts give

genic acid is perhaps formed by shaking o nitropnenyl propiolic scid with H.SO,, but if so, it is decomposed on diluting with water into CO, and

ISATOIC ACID C,H,NO, s. C,H, Anthranil carboxylic acid [230°] S (acetone) 4 4 at 55°

Formation -1 By the oxidation of isatin by CrO, in HOAc (Kolbe, J pr [2] 30, 469) -2 By heating anthranil with chloro formic ether at '30° (Friedlander a Wleugel, B 16, 2227) — 3 By boiling o amido benzoic acid with excess of chloro formic ether (Niementowski a Rozanski, B 22, 1672)

Preparation - (H Kolbe, J pr [2] 30, 469) Isatın (100 g) is powdered and mixed with glacial acetic acid (600 g) A solution of $CrO_3 (200 g)$ in glacial acetic acid (600 g) is slowly added, the temperature being kept below 50°. The flask is left for 12 hours in cold water, and then in water at 50°, and finally at 60° Isatoic acid then be gins to separate as a yellow powder, the separation is completed by pouring into 500 c c cold dilute H₂SO₄ Yield 72 per cent

Properties - Nearly rectangular prisms, which are yellow (through some impurity) when pre pared from isatin Decomposed at 230° ringly soluble in alcohol, ether, and glacial acetic acid, rather more soluble in chloroform and benzene

Reactions -1 Boiled with water it forms o amido benzoic (anthranilic) acid $C_7H_4NOCOH+HO=C_6H_4(NH)CO_2H+CO_2-$ 2 Conc HCl, H₂SO, and dilute HNO, behave in the same way —8 Gaseous HCl passed into an alcoholic solution forms the hydrochloride of o amido benzoicether -4 Aqueous baryta forms, on warming, o amido benzoic acid -5 Ammo nia (aqueous or dry) forms o amido benzamide 6 Aniline at 60° forms the anilide of o amido benzoic acid -7 HNO, (S G 148) forms nitro isatoic acid -8 Nitrous acid gas passed into water, containing isatoic acid suspended, forms Anthranilic acid is (a) nitro salicylic acid doubtless first formed, and this is then nitrated and exchanges NH, for OH -9 Heated with methyl or ethyl alcohol it unites, forming crys talline compounds, carboxylic acids of the methyl or ethyl ethers of o amido benzoic acid.

$$C_eH_4$$
 $CO_{N CO_2H}$
 $CO_{N H CO_2H}$
 $CO_{N H CO_2H}$

The acid CO₂H NH C₆H₄ CO₂Me crystallises in needles [176°], while the corresponding CO,H NH C,H, CO Et forms needles [126°] 10 With benzoyl chloride at 210° it partly reacts

$$-CO_2 + HCl + C_6H_4$$

CO

NBz

forming benzoyl an-

thranil [123°] -11 Bromine forms bromo isatoic acid, which gives with HCl (\$) bromo anthranilio acid [208°] -12 It dissolves in cold dilute NaOH with a blue fluorescence, but on standing the fluorescence vanishes and the solution then contains anthranilic acid (Friedlander a Wledgel, undoxanthic ether (Baeyer, B 15, 780) Isato- B 16, 2227) -18 Phenol at 180° gives phenyl

2-amido benzoate crystallising in needles '70°] (G Schmidt a E v Meyer, J pr [2] 36, 370)—14 Long boiling with glacial acetic acid forms an amorphous compound $C_{34}H_{si}N_{si}O_{si}$, v sl sol ordinary solvents, which yields o amido benzoic acid when heated with HCl or di'ute $H_{si}SO_{si}$ (G Schmidt, J pr [2] 36, 380)—15 Heating with Ac₂O gives acetyl o amido benzoic acid [180°] (S)—16 With hydroxylamine it forms o amidobenzoyl hydroxylamine (E v Meyer a T Bellmann, J pr [2] 33, 19) $C_{si}H_{si}$ + $H_{si}NOH$

mann, J pr [2] 33, 19) C₆H, + H₂NOH N CO₂H = C₆H₄(NH₂)CO NH(OH' + CO₂ - 17 With phenyl hydrazine it forms o amido benzoyl phenyl-

hydrazine C.H. CO.H + PhNH NH.

= C₄H₄(NH₂)CO NPh NH₄ + CO₂.—18 It does not react with boiling di-methyl andline — 19 Pyrocatechin at 180° reacts thus (M a. B).

C,H,(OH)2+C,H,(NCO,H

= CO₂ + C₆H₄(NH₂)CO O C₆H₄OH, forming o oxyphenyl o amido benzoate -20 Boiled with formic acid it forms formyl o amido benzoic acid and a weak base, C31H20N4O4 This crystallises in rhombohedra (from alcohol) It melts at [280°], with decomposition Sparingly soluble in water, alcohol, benzene, and chlo.oform S (ether) 03 at 15°, S (alcohol) 11 at 19° Readily soluble in NaOH, Aq, forming a crystal line salt Its hydrochloride forms prisms, but is decomposed by water Heated with conc HCl at 140° it forms CO2, formic acid, and the hydro chloride of anthranilic acid (M a B) -21 By treatment with PCl, in presence of POCl, a pro duct is got whence methyl alcohol and ethyl alcohol respectively form crystalline products The former gives $C_{16}H_{16}N_2O_3$ [210°], small needles The latter gives $C_1H_{16}N_2O_3$ [170°], With conc HCl at 140° the latter gives needles LtCl and anthranilic acid (M a B) -22 Bleach ing powder suspended in chloroform changes some of the isatoic acid into an isomer [240°], soluble in alcohol, acetone, and benzene dissolves in NH, Aq without forming anthranil amide (unlike isatoic acid), but when HCl is added to the solution an acid [260°] is ppd (M a B) - 23 Heated with glacial acetic acid and bromine (1 mol) it forms brome isatoic acid, but with more bromine CO, is evolved, and di, tri , and te'-a bromo amido benzoic acids are got.

Chloro-isatoic acid CaHaCl

[c 268°] From chloro isatin (10 g), CrO, (20 g) and glacial acetic acid (120 g) as described under bromo isatin (Dorsch, J pr [2] 33, 49)

bromo isatin (Dorsch, J pr [2] 33, 49)

Propertus — Pearly plates (from alcoholether) Sl sol alcohol, acetone, and glacial acetic acid, insol benzene, chloroform, ether, and water

Reactions —1 Conc HCl forms chloro-oamido-benzoic acid [204'] —2 Hot NH, Aq forms the amide of chloro amido benzoic acid

Formation.—By exidation of di chloro-isatin. Properties—Yellow prisms (from alcoholacetone) Melts at 254°-256° with decomposition V soi acetone and glacial acetic acid, sol alcohol and chloroform, v sl sol ether and benzene Boiled with water it partly changes to di chloro o amido benzoic acid, as shown by its violet fluorescence (Dorsch, J pr [2] 33, 51).

Reactions —1 Cone HCl slowly converts it, on boiling, into di chloro amido benzoic acid [224°] —2 With NH,Aq it gives di-chloro-amido benzamide

Bromo isatoic acid C.H.Br

[c 275°]

Formation —1 By oxidising brome isatin.

2 From Br and isatoic acid suspended in glacial acetic acid at 90° (R Dorsch, J pr [2] 33, 32)

Properties —Pearly plates (from a mixture of alcohol and acetone) Sol acetone Sl sol. alcohol and glacial acetic acid Insol water, chloroform, ether, and benzene

chloroform, ether, and benzene

Reactions—1 With boiling cone hydrochloric acid it forms (β) brome amide benzeis
acid C₂H₂Br(NH₂)CO₂H—2 With hot NH₂Aq
it gives brome amide benzamide

Di bromo isatoic acid C_eH₁Br₂CO N CO₂H

[255°] Obtained by oxidising di bromo isatin (10 g) by CrO₂ (10 g) in presence of glacial acetic acid (60 g) as described under bromo Isatin

Properties — Flesh coloured prisms (from alcohol acetone) Sol glacial acetic acid and acetone, sl sol alcohol, chloroform, and benzene, hardly sol ether, insol water Much more stable than bromo isatoic acid

Reactions—1 Boiled for a long time with cone HCl it gives off CO_r leaving di bromo camido benzoic acid—2 It does not dissolve in NH₂Aq But if heated with it at 100° for a long time it forms di bromo amido benzamide C₄H₄Br₄(NH₄)CO NH₂ [197°]

C,H,(NO,)NO CO,H. Nitro-isatoic acıd [220°-230°] Formed by the action of HNO. (5 G 148) on isatoic acid Insol water and ether, sl sol alcohol Crystallises from equal parts of alcohol and acetone in pearly plates It resembles isatoic acid, splitting up readily into CO, and nitro-o amido benzoic acid, when boiled with HCl or even with water Nitro-isatoic acid is converted by aqueous NH, into nitro amido benzamide By Sn and HCl it is reduced to diamido benzoic acid, CO, escaping Bromine (in glacial acetic acid) converts it into mono, di-, and tri- nitro-amido benzoic acids (q v)

Methyl-isatoic acid C.H.Me

Preparation — Methyl-isatin (10 g) is mixed with glacial acetic acid (60 g) and cooled well while a mixture of CrO, (21 g) in glacial acetic acid (60 g) is slowly added — After 12 hours at 0° the mixture is heated for 2 hours at 40° and thin to 70°— It is poured into water containing H,SO,, and the yellow powder crystallised from absolute alcohol (Panaotović, J pr [2] 31, 122, 33, 58)

Properties -Pale-yellow crystalline plates

1256°]

(from boiling alcohol) or trimetric columns (from acetone) At 245° it suddenly increases in bulk, but it melts above 300°, giving off CO, V sl sol. water, readily sol boiling alcohol, ether, benzene, and chloroform

Reactions -1 Is more stable than isatoic scid, not being decomposed by dilute mineral acids.—2 HNO_s (S G 148) dissolves it in the sold After 12 hours water is slowly added, and the pp crystallised from benzene It forms pale yellow trimetric plates of nitro methylisatoic acid [175°] This acid is reduced by Sn and HCl to a diamido-toluic acid -8 Warmed with HCl (SG 12), CO2 is given off, and the hydrochloride of amido p toluic acid [207°] formed —4 Warmed with NH, Aq it gives the amide of amido toluic acid [178°] -5 With aniline in alcohol it forms the corresponding anilide [243°]—6 With phenyl hydrazine it forms the corresponding hydrazide—7 With MeOH at 180° it forms methylic amido-toluste

Methyl-isatoic acid C.H.NO. se **CO** C.H.Me [226°] Formed by boiling ∕ү со'н

amido - toluic C₆H₃Me(NH₂)CO₂H acid [5? or 3? 1 2] with chloro formic ether (Niemen towsky a Rozansky, B 22, 1675) Needles or scales, v sl sol benzene and ether, sl sol alcohol Decomposed on fusion Acids and Acids and alkalıs decompose it into CO, and amido toluic acid [177°]

Isomeride of isatoic acid & Anthroxanic

ISATYDE C16H12N2O4 Produced by the reduction of isatin by zinc and dilute H2SO, by alcoholic ammonium sulphide, or by zinc dust and HOAc (Laurent, A Ch [3] 3, 382, A 72, 285, Erdmann, J pr 24, 15, 25, 438, Baeyer, B 12, 1309) Formed also by atmospheric oxi dation of an aqueous solution of dioxindole (Baeyer a Knop, A 140, 10) White powder, with slightly greyish tint, almost insol water, v sl sol boiling alcohol and ether Separates from boiling alcohol in minute scales Decomposed by heat, becoming at first violet-brown Alcoholic potash forms isatic acid, indin, and other products

 $\textbf{Di-chloro-1satyde} \ \textbf{C}_{16} \textbf{H}_{10} \textbf{Cl}_2 \textbf{N}_2 \textbf{O}_4$ Formed by the action of ammonium sulphide on chloro-White powder, crystallisable, insol cold, v sl sol hot, water, m sol boiling alcohol, sol. hot aqueous potassium sulphide 180° it is resolved into chloro-isatin and chloroındın Boiling aqueous or alcoholic potash forms potassium chloro isatate and the salt $C_8H_3Cl(NH_2)$ CH(OH) CO_2K

Tetra-chloro-isatyde C16H8C14N2O4 Produced by the action of ammonium sulphide on di-White powder, insol water chloro-ısatın De composed by heat into di-chloro isatin and dichloro indin Alcoholic potash forms di chloro ısatın and dı chloro-o amido-a-oxy phenyl acetic (di-chloro hydrindic) acid

Tetra-bromo-isatyde $O_{10}H_{0}Br_{4}N_{2}O_{4}$ From dibromo isatin and ammonium sulphide Resolved by heat into di-bromo-isatin and di-bromo-

Thio-isatyde C16H12N2O2S Formed by slowly adding alcoholic potash to an alcoholic solution of di thio isatyde (Laurent, A Ch [8] 8, 463)

White crystalline powder May be crystallised as minute rectangular scales from hot alcohol Insol water, v sl sol boiling alcohol and ether. Cold potash forms indin and other products Hot potash forms the hydride of indin

Di-thio-satyde C₁₆Hi₁₂N₂O₂S₂ When H₂S is passed into a cone alcoholic solution of isatin the liquid becomes pale yellow and on cooling deposits crystals of sulphur and of isatvde The filtrate when mixed with water deposits di thioisatyde (Laurent) Yellowish grey amorphous powder Decomposed by heat Insol boiling water, v sol warm alcohol and ether Ammo Lum bisulphite converts it into 'ammonium sulphisatanite' NH₄C₈H₆NSO₄ aq, which crystallises in large pale yellow tabler v sol water, m sol alcohol

D1-bromo-di-th10-isatyde C10 H10 Br2 N2O S2. Formed, together with di bromo tri thio isatyde, when H2S is passed into a boiling anoholic solution of bromo isatin (Gericke, Z 1865, 595). Yellowish white powder, insol hot water, sol hot alcohol and ether

Di-bromo-tri-thio-isatyde C₁₆H₁₀Br₂N₂OS₃

Formed as above Yellowish white powder Isatane C₃₂H₂₈N₄O₄ Formed, as a white pp, when di-thio isatyde is boiled with a solution of ammonium bisulphite (Laurent, J pi 28, 346) Formed also by the action of sodium amalgam on an acid solution of isatin (Knop, J pr 97, 65) Small white cubes (from ether or hot alcohol), Decomposed by hot alcoholic insol water potash into dioxindole and indiretin holic solution gives with ammoniacal AgNO, a

white pp of Ag,C,,H,2,N,O, ISETHIONIC ACID C,H,SO, 16

HO CH, CH, SO, H Oxy ethane sulphonic acid Sulphonic acid of ethyl alcohol Mol w 126

Formation -1 Discovered by Magnus in 1833 (P 27, 378, A 6, 163) as a product of the action of SO, on alcohol or ether Hence it is found among the residues in the preparation of ether -2 By boiling ethionic acid with water (Magnus, A 32, 251) -3 By the action of SO, on barium ethyl sulphate (Meves, A 143, 196) 4 By the action of nitrous acid on taurine NH₂CH CH₂SO₃H (W Gibbs, Am S [2] 25, 30) 5 By heating chloro ethyl alcohol (chlorhydrin of glycol) with aqueous Na, SO, at 175° (Coll mann, A 148, 101)—6 By heating ethylene oxide with aqueous KHSO, at 100° (Lrlenmeyer a Darmstadter, Z 1868, 342)—7 Probably formed by boiling ethylene bromide with aqueous Na_2SO_3 (James, C J 43, 44) -8 P_J oxidising thio glycol HO CH2 CH2 SH with nitric acid (Carius, A 124, 260)

Preparation —SO₃ is added, with shaking, to an equal weight of ether at 0° As soon as a sample mixed with water gives a heavy oil the whole is poured into water and the ethyl sulphate washed with water till neutral, dried over H2SO4, treated with its own weight of SOs, and then poured into water The two aqueous liquids are boiled for a long time to decompose ethionic acid, and then neutralised by baric carbonate, on evaporating baric isethionate is got (R Hubner, A 223, 212)

Properties - Viscid, strongly acid syrup, which gradually dries up to a deliquescent radio crystalline mass Is not decomposed at 150°, but blackens at a higher temperature Its salts are not decomposed by boiling with vater. and may even be heated to 200°, above which temperature, however, they lose water and change to di isethionates Potash fusion gives potassium carbonate, oxalate, sulphate, and sulphite Berthelot (Z 1869, 622) obtained acetylene, K2803, and hydrogen PCl, yields CH2Cl CH, SO2Cl, which is converted by heating with aqueous ammonia into taurine (Kolbe, 112, 241) Chromic and oxidises isethionic acid to sulpho acetic acid CO2H CH2 SO4H

Salts -NH, A' octahedra [130°] (Strecker), [185°] (Seyberth, B 7, 391) At 235° it changes to ammonium di isethicuate (Carl, B 12, 160-) -KA' rhomboidal prisms, melting between 300° and 350° witho t loss of weight May be crystallised from alcohol —BaA', transparent six sided plates [32^o] V sol water S (60 pc alcohol) 6 at 14° —CuA', 2aq pale green prisms AgA very hygroscopic pearly needles

Double salts with Et, SO, (Engelcke, A 218, 270) From NaA', H2SO4, and alcohol, and conversion into barium salt BaA'2Et,SO4(?) -

NaA'Ft,SO.

Double salt with Me₂SO₄—NaA'Me₂SO₄, Silky monoclinic tables (from alcohol), very hygroscopic Decomposed by water at 80°, thus

C,H,(OH)SO,NaMe SO,+2H O $= C_1H_1(OH)SO_1H + 2MeOH + NaHSO_1$

EtO Ch, CH SO, H Ethyl derivative S G 21 1 359 Sulphonic acid of ether sodium salt is obtained by the action of chloro ethane sulphochloride on excess of NaOEt (R Hubner, A 223, 218) Also from CH₂Cl CH₂ SO, Na and NaOLt The free acid is got by boiling with water the product obtained by acting with H2S on the (molecular?) compound of its lead salt with lead ethyl sulphate It is a syrup

Salts —NaA' Plates S (alcohol) 27 at 15° —NaA' aq Columns —BaA' aq —ZnA 26aq

Hygroscopic plates -CuA'.6aq

Double compounds with the salts of ethyl sulphuric acid EtSO,H Got by adding H SO, and alcohol to EtO CH CH2 SO, Na, filtering from Na₂SO₄, and neutralising with a metallic carbonate. The general formula is C2H3SO4H, C H3O C2H4 SO4H or C H14S2O4H, e q BaA" aq Sılky scales — (NH₄). A'₁A'₂.—PbA', A'₂ — Na A'₁A'₂ aq — Zn A'₁A'₂ 5aq — CuA'₁A'₄ 4aq These salts are very soluble in water The free acid splits up on boiling with water, in the follow ing manner C₂H SO₄H,EtO C₂H₄ SO₃H + H₂O

= EtO C₂T₄SO₂H + H₂SO₄ + EtOH Ethyl ether HO CH, CH SO₂Et From AgA' and EtI (Stempnewsky, J R 1882, 95)

Ethyl derivative of the ethyl ether EtO CH. CH. SO, Et SG 15 1168 (impure) From CH2Cl CH SO Cl and NaOEt in ether Not obtained quite pure

Benzoyl derivative BzO CH2 CH2 SO, H From potassium isethionate and BzCl (Engelhardt a Latschinoff, Z 1868, 235) -KA' lets, v sol boiling water, sol hot alcohol-BaA', aq Large thin tables, m sol cold water,

sol boiling alcohol

Chlorede HOCH, CH, SO,Cl Probably formed, together with CH₂Cl CH₂SO₃H and CH₂CH₂O SO₂Cl, by the action of SO₂ on ethyl chloride, or of ClSO, H on ethylene (Purgold, B 6, 504) Excess of SO, converts it into the

chloride of cthionic scid (Claesson, J pr [2] 19.

Di-isethionic acid O(CH, CH, SO, H), Di phonic acid of ether The ammonium salt of sulphonic acid of ether this acid is obtained by heating ammonium isethionate to 210° (Carl, B 12, 1604) — (NH₁)₂A" [198°] Slender leaflets or scales, v e sol, water —BaA"aq prismatic tables Formed by water —BaA"aq prismatic tables heating barium isethionate to 200° (Carl, B 14,

ISINGLASS v PROTEIDS, Appendix C.

I80-Compounds whose names begin with 180 are usually described either under the name to which iso- has been prefixed or else under their systematic names as described in the Introduc tion to Articles Relating to Organic Chemistry,

ISOMERISM. Even a superficial reader of chemical literature will soon become aware that the term isomeric and the kindred expres sions allotropic, metameric, and polymeric are by no means always used in consistent senses, and he will have considerable difficulty in clearly realising their exact and relative import, it, therefore, appears desirable to discuss the mean ings of these terms, especially from the historical side, and as far as possible to define the sense in which they are severally applicable. The follow ing extracts from the article Isomerism in the first edition of this Dictionary, vol in p 415, 1865, by J A Wanklyn, serve to show what views were held at the very outset of the period when the investigation of isomeric substances began largely to engage the attention of chemists

'Isomerism.-This term is derived from look equal, and $\mu\epsilon\rho\sigma_0$ a part, and its employment by chemists is an expression of the fact that very different chemical compounds soon of the 1800 that very different chemical compounds have sometimes identically the same ultimate composition. Two or more different bodies which are composed of the same elements (i.e. which have the same proportions of these elements (i.e. which have the same proportion) are said to be tomeric. Isomerism is sometimes used in a nerrower sense, being made to signify equality of molecular weight, as well as identity in percentage composition. When the compounds have the same percentage composition but different molecular weights, the term polymeric is employed. Thus there are the terms Isomeric (in its wide sense), signifying that the different bodies have the same percentage composition, Polymeric, signifying that these different bodies have the same percentage composition, but different molecular weights, Isomeric (in its restricted sense), sometimes called Metameric, signifying that the bodies have the same percentage composition, and likewise the same molecular weight.

As examples, Wanklyn then cites butyric acid, ethylic acetate, aldehyde, and ethylenic oxide as esomeric compounds, using the term in its widest sense of these butyric acid and ethylic acetate are said to be polymeric with aldehyde and ethylenic oxide, butyric acid being isomeric (in the restricted sense) or metameric with ethylic acetate, aldehyde and ethylenic oxide being also metameric compounds Subsequently, throughout his article, Wanklyn uses the term isomeric in its wide sense, substituting the term metameric for isomeric used in its restricted sense, thus he speaks of methyl, the simplest alcohol radicle, as metameric with ethyl hydride (I is article was written at a time when Schorlemmer's investigation was not fully recognised as affording proof of their identity), he points out that several metameric hexanes are possible, and even quotes 'as a very remarkable example of metamerism' the different varieties of tartaric acid and racemic acid

The term allotropy is made use of by Wank lyn in an unusually wide sense. Thus he says—

'Closely related to the term isomerism is the term allotropy Both of them have reference to the same substantial fact, viz that different substances have sometimes the same ultimate composition, but they differ in their manner of stating it. Isomeric and allotropic are in fact complementary terms, "isomeric" being employed to predicate identity of composition between different bodies, whilst "allotropic" expresses difference between bodies of identical composition. Such being the force of these words, there is a certain propriety in their usage thus, whilst it is correct to say "butyric acid and acetic ether are isomeric," it should be "there are allotropic bodies of the formula C.H.N". The same reason which enjoins the use of allotropic in this case prescribes it in the instance of single elements thus, for example, we read of "allotropic in this case prescribes it in the instance of single elements thus, for example, we read of "allotropic in this case of isomerism occurring in in organic chemistry are usually described by employing the word allotropy or allotropic, while the reverse obtains in organic ohemistry. This may be partly ascribed to there being always a very wide difference—or else no difference at all—in the composition of any definite inorganic substances, and hence the fact of identity or non identity of composition being so easily ascertainable, it is implied in the form of expression, whilst the fact of difference of properties alone needs to be made the subject of formal predication. Among organic bodies, on the other hand, it continually happens that the differences of composition are quite decided, and yet so very minute as to tax the utmost equite decided, and yet so very minute as to tax the utmost equite decided, and yet so very minute as to tax the utmost equite decided, and yet so very minute as to tax the utmost equite decided, and yet so very minute as to tax the utmost equite decided, and yet so very minute as to tax the utmost equite decided, and yet so very minute as to tax the ut

He then cites the olefines as examples of polymerism, and afterwards discusses numerous cases of metamerism, several of which were referred to above

Under the heading Isomers among Inorganic Substances the following interesting passages occur at the conclusion of the article —

'As before remarked, the instances of inorganic isomerism are usually called instances of allotropy—isomeric substances and allotropic substances being nearly equivalent expressions. The elementary substances themselves offer many examples of isomerism. Ozone and oxygen are isomeric bodies. Experiment has shown that the molecular formula for ozone is higher than that for oxygen, but how much higher remains an open question. Sulphur, phosphorus, carbon, and many other elements present somehat similar examples of allotropy or isomerism. Inorganic compounds, such as the various forms of silicio acid, of sesquioxide of thron, of sesquioxide of chromoum, of alumina, must be classed among substances afording examples of isomerism. The explanation of the existence of isomerism will have become sufficiently clear from the course which has been followed in describing the different examples of it. "It is of consequence how the atoms of a compound are arranged, as well as what kind of atoms they are, and hence there may be very many totally different substances composed of the same ultimate atoms. This is in fact the whole philosophy of isomerism.

The definitions given in Kekulé's Lehrbuch (1867) are substantially the same as those adopted by Wanklyn, but he specially draws attention to the existence of compounds isomeric in a restricted sense, which, according to the state of knowledge of the time, were to be represented by the same rational formulæ, although they either were possessed of different properties—as in the case of the CipHie hydrocarbons and of maleic and tumaric acids, or they were in all essential te spects chemically identical but physically different—such as the tartanc acids, mucic and such as these latter, in fact, gave rise to the re-

cognit on of a distinct kind of isomerism, termed physical isomerism

In the latest edition of Watts' Founes by Tilden (1886), polymerism is included under isomerism, but compounds of the same mole cular weight are sub-divided into (1) metameric bodies, namely, those which exhibit dissimilar transformations under similar circumstances propionic acid, methylic acetate, and ethylic formate are quoted as examples, and (2) isomeric bodies, strictly so-called, namely, those which exhibit the same or closely similar decompositions and transformations when subjected to the action of the same reagents, such as the C_{1e}H_{1s} hydrocarbons, the glucoses, the tartaric acids, &c

It will be noted how incompatible are the definitions given by Wanklyn and in Fouries of the term metameric, it has, however, undoubtedly been customary of late years so employ the term metameric in the sense indicated in Fouries

In M'Gowan's translation of Bernthsen's Organic Chemistry (1889), the most modern book of its kind, polymerism is not reckoned under isomerism, but the definition given of metamerism is on the whole more in agreement with that quoted from Watts' Fouries, after it has been explained that ethers such as methyl amyl ether, ethyl butyl ether, and dipropyl ether are isomeric, we read—

'Such isomerism which depends upon the grouping together by a polyvalent element of alcohol radioles which are individually unequal, but the sum of whose elements taken together are equal, is called metamerism. One of the alcohol radioles may here be replaced by hydrogen. Alcohols and ethers containing an equal number of carbon atoms are therefore metameric.

We further learn that the isomerism of the higher paraffins, since it is based upon the dis similarity of the carbon chains, is often termed chain isomerism, that the isomerism between ethylene and ethylidene chlorides, or between primary and secondary propyl alcohols, as it depends upon the difference in position of the substituting halogen or hydroxy in the same carbon chain, is termed isomerism of place or position, and that there is the third kind of iso merism, viz metamerism But obviously two different kinds of relationship are thus included under metamerism that of position isomerism, which obtains among the ethers themselves, which are necessarily all compounds of one primary type, and that which obtains between the typically different 'equi moleculai' alcohols and ethers, or true metamerism, if the Watts Fownes definition be adopted

If we consider the origin of the four terms under consideration we find that they were all devised by Berzelius The term isomeric is proposed in his Jahresbericht, handed in to the Swedish Academy of Sciences, March 81, 1831 (cf Wohler's German translat on, 1862, ii pp 44-8), in the following words —

'Da es nothwendig ist, für gegebene Ideen bestimmte, und so viel wie möglich cor sequent gewählte, Ausdrücke zu besitzen, so habe ich vorgesohlagen, Körper von gleicher Zusammensetzung und ungleichen Rigenschaften isomerische zu nennen, vom griechischen crousepig (aus gleichen Thellen zu sammengesetzt)'

In the next volume of his Jahresbericht (Wöhler's translation, 1838, p 63) he gives a

further all important defin.tion of the use he would make of the term, thus —

'Um jedoch nicht Erscheinungen von nicht vöillig gleicher Art mit einander zu verwechseln, ist es nothwendig den Begriff vom Worte Isomerie genau zu bestimmen. Ich erwikhnte dass ich darunter Körper verstelt, die aus einer gleichen absoluten und relativen Atomen-Ansahl derselben Elemente zusammengesetzt sind und gleiches Atomgewicht haben womit nicht der fall zu verwechen ist, wo die relative Anzahl der Atome gleich ist, die absolute aber ungleich. So ist z B die relative . nzahl von Kohlenstoff und Wasserstoff-Atomen im ölbilde .den Gas und im Weindi absolut gleich, allein in einem Atom vom Gase eind bloss 1 Atom Kohlenstoff und. 2 Atome Wasserstoff enthalten, CH_w wihrend dagegen im Weindi 4 Atome Kohlenstoff und 8 Atome Gleichheit in der Zusamn nsetzung, bet Ungleichheiten in den Biyenschaften beseichnen zu können, möchte ich für diese Körper die Benenung polymerische (von πολυτ, mehrere) vorschlagen.

It will be clear from this quotation, especially from the words which I have italicised, that Berzel is never intended that polymerism should be regarded as a form of isomerism

The following passage from the same source clearly exhibits Berzelius's intention as to the use which should be made of the term metameric—

'Allein es gibt noch andere Verhältnisse, wo Körper, in eigentlichen Sinne des Wortes, isomerisch scheinen, d. h. dieselbe relative und absolute Atomenanshi derselben Elemente enthalten konnen, ohne espedoch volltidadig zu zein Ein solcher Fall ist wenn K. riper aus zwei zusammengesetzten Atomen der ersten Ordnung bestehen, die sich auf verschiedene Weise gegen einander un zeen und in Folge dessen ungleiche Korper bilden konnen, s. B. Snå(SnOSO_a) schwefelsaures Zinnoxyd, enthalten eine gleiche absolute und relative Annahl derselben Elemente, und haben disselbe Atomgewicht, können jedoch nicht als ein und derselbe Korper betrachtet werden. Bei solchen Körpern ist es der Fall, dass wenn sie eine gewisse Zeit lang bestanden haben, oder wenn die Temperatur geändert wird, eine Umlegung der Bestandthele in ihnen vor sich geht, ohne dass etwas hinzukommt oder davonweggeht, und dass daurch eine anders beschaffene Verbindung entsteht, welche Verlinderung nicht selten von einer Temperatur Erböhung begleitet ist. Um solche Fälle bestimmt von Isomerie zu unterscheiden, können wir dafür die Beselchnung metamerische Körper gebrauchen (von µera in der selben Bedeutung wie in McLamorphose)'

Berzelius also cites cyanic and cyanic acids, which were not then regarded as compounds of different molecular weight, as instances of meta meric compounds, regarding the conversion of the latter into the former on heating as a case in which 'die Cyanicsaure von einem zusammengesetzten Atom der ersten Ordnung, oder einem Oxyd eines ternaren Radicals, in ein zusammengesetztes Atom der zweiten Ordnung, nämlich in Cyansaure mit chemisch gebundenem Wasser übe geht' Cyamelide, into which cyanic acid spontaneously changes, and cyanica acid, in Berzelius's opinion, were (wenigstens vor läufig) isomeric oxides of the same radicle

It is clear therefore that the conception involved in the definition of metamerism given in Watts' Founes, and in the first edition of this dictionary, is scarcely in conformity with the use of the term by Berzel'us, indeed, in 1840 he speaks of ethylic formate and methylic acetate as isomeric. From the example afforded by the two tin compounds, as well as from the explanation given of the nature of the change from cyanura to syanic acid, it is to be supposed that the compounds which he intended should be included in the category of metameric substances were such as we should now term typically different, and with this conclusion the modern practice is in Vog. III.

distinct accord, yet the modern and the original application of the term are far from being equivalent, the meta- in metamorphosis denoting change the conversion of the one metameride into the other being expressly referred to, it would appear, in fact, that Berzelius distinctly intended to apply the term to those compounds which are capable, in modern phraseology, of undergoing 'isomeric change,' and perhaps to these alone

It was not until 1840 that Berzelius proposed to substitute the term allotropic (von allotropic swelches bedeutet, von ungleicher Beschaffenheit, BJ 1841 inorg sec p 13) for isomeric, in the cases of the existence of modifications of elementary substances. He appears, however, to have contemplated its extension to compounds, judging from the following passage.

'Es kann dann mehr als eine Ursache von dem was wir Issemerie nennen, geben, namilch (1) Allotropie, wenn namilch das vorhin angeführte Beispiel von den beiden Schwefelkiesen darauf beruht, dass der eine davon Sa und der andere Sø enthält , (2) die ungleiche relative Lage der Atome in der Verbindung , und (3) kann sowohl Allotropie als ungleiche Stellung der Atome in gewissen Fällen zugleich stattfinden '

The existence of compounds containing allotropes of one of the constituent elements is distinctly suggested here, but there is nothing to indicate in what way allotropes may be regarded as related, that Berzelius had realised that the re lation might be that of polymerides would appear to follow from his reference to Frankenheim's experiments on sulphur, in which it is suggested that the different modifications of sulphur form corresponding gases, and that the dark yellow gas of sulphur, weighing thrice as much as sulphur gas should according to calculation, is not that of the modification occurring in the ordinary sulphur compounds (v Allotropy, vol 1 p 128 the view here taken is somewhat wider than that adopted by Prof L Meyer in that article)

As the term allotropic has a general signification, implying only another condition, and involves no assumption either regarding the molecular weights of, or as to the nature of the relationship which obtains between, the allotropes, it may with great advantage be employed in place of the term isomeric used in a wide sense, this latter term being preferably restricted to those cases in which there is the very closest similarity in structure Polymerism, metamerism, and isomerism may in fact all be regarded as varieties of allotropy, there is certainly no reason why carbon compounds should be considered apart from those of other elements, or from elementary substances

The rational formulæ which are ordinarily made use of are condensed symbolic expressions affording more or less complete information as to the characteristic chemical properties of the compounds which they represent, especially with regard to the manner in which they are formed, and in which they undergo change when submitted to the action of various agents, and equimolecular allotropes which differ either in their mode of formation or in their behaviour under similar circumstances are, as a rule, necessarily represented by different rational formulæ The formulæ devised for any class of compounds, however, will vary according to the views which

ISOMERISM.

are held as to the valencies of the constituent atoms At present, formulæ are almost invariably constructed on the hypothesis that the several units of affinity—the valencies—of a polyad atom, such as that of carpon, nitrogen, or sulphur, are of the same value and have identical functions, this conclusion being based on the fact that lone of the simple derivatives of methane, ammonia, &c . exist in a greater number of modifications than the hypothesis requires But it cannot be too positively stated that, notwithstanding the extent to which experimental investigation has been carried, we are yet but on the threshold of the temple in which the mysteries of valency are enshrouded The valency of the hydrogen atom is determined ex hypothesi to be unity, and when the facts generally are passed in mental review, it would seem that this conclusion is no mere hypothesis, it is not improbable also that the valencies of the atoms of at least the majority of metallic elements are invariable, but the valencies of the atoms of the non metals are apparently variable By valency is here understood atom fixing power

Most discussions on valency are dialectical rather than scientific, in consequence of our powerlessness at present to decide what constitutes 'a valency,' the deduction from Faraday's law of electrolysis, to which Helmholtz has directed the attention of chemists (Faraday lect, C J Trans 1881 p 277), that definite, as it were atomic, charges of electricity are associated with the atoms of matter—that a monad bears a single charge a dyad two, a triad three—is the only approach yet made to a theory of valency, but hitherto chemists have avoided the discussion of the subject from this point of view

Oxygen and sulphur, nitiogen and phosphorus carbon and silicon, form gasifiable hydrides, from the composition of which we infer that the atoms of these elements are divalent, trivalent, and tetravalent, respectively, in the case of carbon and silicon there is no reason to suppose that either element ever manifests a But both water and ammonia higher valency readily combine with other molecules the form ation of such compounds from water is rarely interpreted as evidence of the possession by oxygen of the power of acting as a tetrad, but the water molecule is usually supposed to func tion in some occult manner as a whole, and to enter into a state of 'molecular combination' dif ferent from that of 'atomic combination' in which its constituent atoms exist The formation of ammonium compounds, however, is more usually regarded as due to the manifestation of a higher degree of valency by the nitrogen But there is no good reason for explaining the behaviour of oxygen in one way, and that of nitrogen in an other

The question to be decided is, whether a given element may possess two or more degrees of valency, and whether the so-called atomic and molecular forms of combination differ merely in degree and not in kind Or, to put it in

anothe. way —is the number of atomic charges ass clated with a given atom invariable or variable, is it possible for an oxygen or sulphur atom, for example, to carry more than two, or for a nitrogen or phosphorus atom to carry more than three, charges? The writer has endeavoured to explain the exhibition of varying degrees of valency on the assumption that, while the number of charges which any given atom can carry is invariable, a single charge may operate in promoting the union of more than two atoms (cf P M January 1888), that in water, for example, the two charges of the oxygen atom are not fully engaged by those of the hydrogen atoms, and that consequently the oxygen atom is still possessed of a certain amount of residual affinity It may be contended that, according to this hypothesis, a compound formed of say trimethylamine and ethyl iodide, Me,N IEt, would be an allotrope of a compound of ethyl dimethylamine and methyl iodide, EtMe,N MeL The most careful experimental study of such compounds (cf V Meyer a Lecco, Ber 9, 309, Ladenburg, Ber 9, 561, 1634, Klinger a Class son, A 243, 193) has been made, however, with the result that, in the case of ammonium compounds, it is immaterial in what order or manner the radicles are introduced, and the same is true in the case of sulphine compounds hence it is supposed that nitrogen has five, and sulphur four, affinities of equal value But this by no means follows, as the occurrence of 'isomeric change' in such cases is in the highest degree probable-the compound abcNId may alone be the stable form into which the allotropes abd NIc. acdNIb, bcdNIa, all spontaneously undergo con version immediately on formation little doubt that such 'isomeric changes' occur far more frequently than is commonly supposed, and it is most important that the possibility of 'isomeric change' should be very carefully kept in view in determining the constitution of com pounds from the study of their behaviour in a limited number of interactions As valency cannot be determined from any a priori con siderations, and can only be deduced from the knowledge of the structure of the compounds of the elements whose valency is to be determined, it is obvious that the structure of a substance must be inferred from the widest and most care ful study of all its properties the study of the relationships of allotropic substances is in fact inseparable from that of valency, and the con verse is equally true

In the case of 'unsaturated' carbon compounds, it has been customary of late years to represent the affinities not engaged by other elements as saturating each other thus, ethylene is formulated as H₂C CH₂, acetylene as HC CH Thomsen's determinations of the heat of combustion of ethylene and acetylene in comparison with those of saturated hydrocarbons, as well as the general behaviour of such unsaturated compounds, may, however, be held to favour the view that the carbon atoms are possessed of free affinities, as expressed by the formulæ H.O...

HC— Although the discussion of this question excited considerable attention a few years ago, it has latterly almost entirely fallen into

^{&#}x27; It appears to me that the term valency must at present be used in a perfectly general sense, and that we cannot restrict our attention to the consideration of gaseous compounds (* EQUIVALENCY) in the case of gase, the problems are for the most part of a very simple kr d, and rarely excite differences of opinion, liquids and solids, however, present problems of great complexity

oblivion, but as very many of the cases of anomalous isomerism, of which an explanation is required, occur among compounds of the ethylenic type, it is one of considerable importance. The possibility of the two forms of com-

bination pictured by the expressions # and

 H_2C- should also be taken into account, espe H_2C-

cially in the case of ethylenic derivatives

Among the more recondite problems of valency requiring mentice is that relating to the number of carbon atoms which form closed chains or ring. It is now regarded as well established that, in addition to the six atom ring of benzene, five atom rings also exist, indeed, their formation apparently takes place with peculiar readiness, the existence of both three-and four atom rings is now also generally held to be established, chiefly in consequence of the researches of W H Perkin, jun (cf C J Trans 1885 801, et seq) The hydrocarbon obtained by the action of sodium on trimethylene bromide, BrCH CH, CH, Br, is almost universally assumed to be the simplest compound of the land trimethylene Hard trimethylene has the simplest compound of

the kind, trimethylene $\frac{H_{C}C}{H_{C}C}$ CH₂, as shown by Freund, its discoverer, this hydrocarbon has the remarkable property of being reauly absorbed by a solution of hydrogen iodide, forming normal propyl iodide, although it is acted on with extreme slowness by bromine By the action of ethylenic bromide on the disodium derivative of ethylic malonate, Perkin has obtained an acid which he regards as a trimethylenedicarboxylic

acid $\frac{H_2C}{H_1C}$ >C(COOH)₂, and by employing tri methylenic bromide in place of ethylenic bromide, he has prepared what he regards as tetramethyl

enedicarboxylic acid (CH_2-CH_2) both acids $(CH_2-C(COOH)_1)$

closely resemble the hydrocarbon in their beha viour with bromine and halhydrides The casy resolution of closed carbon chains by halhydrides in this manner, however, is altogether without precedent in the case of five and six atom car bon rings, at all events, which, as a rule, cannot be split by means of halhydrides, but are fre quently resolvable by bromine, their behaviour is more nearly akin to that of five atom rings, such as those of furfuran and indole, which also resist the action of bromine, but are resolvable by treatment with agents which are commonly regarded as weaker than bromine (the formation of pyridine derivatives from pyrrole and of quinoline derivatives from indole, which appears to involve the resolution at some stage of the ope ration of the five atom rings, is contemplated in this statement) The alternative formula for trimethylene, if it be not a closed chain hydro carbon, is CH, CH, CH, which represents it as a compound in which two terminal carbon atoms are each possessed of a single free affinity, the possibility of the existence of such compounds has not yet been contemplated by chemists, ex cepting myself It is conceivable, I think, that such a compound would be attacked by bromine with difficulty, in consequence of the two un-

satisfied carbon atoms failing to assist each other in separating the constituent atoms of the bromine molecule and the impossibility of a 'conducting chain of molecules' being formed between the carbon atoms, as bromine is a dielectric, as solutions of the halhydrides are electrolytes of low resistance, such a conducting chain might, however, be formed in their case, and the requisite electrolysis of the halhydride molecule could thus occur According to Thomsen, trimethylene has a higher heat of combustion than propylene, CH, CH CH2, judging from the analogy afforded by benzenoid compounds, it is to be expected, however, that the closure of the chain involved in the formation of the three atom ring would be attended with a considerable loss of energy, and that propylene would, therefore, have the higher heat of combustion its behaviour with bromine certainly justifies this view The confirmation of Thomsen's statement thus becomes of extreme importance It is a noteworthy fact that ethylenic oxide, according to Thomsen, also has an exceptionally low heat of formation, and that this ob server has proposed to represent it as a dimethylene oxide of the formula CH2O CH2 Ethylenic oxide as represented by the conventional formula bears a similar relation to trimethylene that furfuran bears to pentamethylene, thus

Thomsen's formula for ethylenic oxide is mad missible, as it indicates a severance of the carbon atoms, if, however, the formula were written CH₂CH. O, it would correspond to that given above to trimethylene, Thomsen's observations that both ethylenic oxide and trimethylene have an exceptional heat of combustion may there fore be regarded as mutually confirmatory. It is also to be noticed that the compound formed from ethylenic bromide and a sulphide is not the corresponding sulphide, but the polymeride

CH₂—S—CH₂
hereof | | If an open chain formula
CH₂—S—CH₃

be assigned to trimethylene, Perkin's tri- and tetramethylene derivatives must also be represented by open chain formule. Perkin has fully discussed this question, and has pointed out the improbability attaching to such formule. The evidence does not appear to be sufficient, however, to permit of a final decision being arrived at with regard to so difficult a question.

Finally, it is necessary to refer to a problem closely akin to the two previously considered, viz that relating to the distribution of the spare affinities of the carbon atoms in closed chains, of those affinities, that is to say, which are not engaged in the formation of the ring, or in re taining the hydrogen atoms. This problem is chiefly of importance in discussing the structure of benzenoid hydrocarbons and their derivatives of the various formulæ proposed for benzene, that of Kekulé always has been, and still remains, the most popular, but it is open to the serious objection that it represents benzene as a compound containing three pairs of carbon atoms in the same condition as the pair in ethylene. Dewar's for-

mula is open to a similar objection 'The prism formula of Ladenburg and the diagonal formula of Claus cannot be objected to on this ground, but are open to criticis n in many other respects, and in the light of Von Baeyer's recent researches on the reduction products of terephthalic acid of A 245,103, 251,257) these formula are generally regarded as finally disposed of (cf Miller, C. S Trans 1887 208) A symbol proposed by the writer in February 1887 (cf P. M), and a year later also by Von Baeyer (A 245, 122), appears to be exempt from the deficiencies which characterise previous formulae, but it embodies somewhat unconventional conceptions, and therefore has not yet attracted attention The

84

symbol in question has been very happily

termed the centruc formula by Von Baeyer, he expressly states that this formula is to be under stood to indicate that 'die 6 Kohlenstoffvalenzen des Benzols sich sattigen, ohne dadurch drei Verkettungen der Kohlenstoffatome zu bewirken' (A 251, 285)—one valency of each atom is directed towards the centre of the ring, and these valencies mutually paralyse each other (A 245, My own words were 'Of the twenty four affinities of the six carbon atoms twelve are en gaged in the formation of the six carbon ring, while the remaining six react upon each other, acting towards a centre as it were, so that the affinity may be said to be uniformly and sym metrically distributed I do not consider that, apart from its connexion with the other carbon atoms owing to their association in the ring, any one carbon atom is directly connected with any other atom not contiguous to it in the each individual carbon exercises an influence upon each and every other carbon atom there is an excess of affinity beyond what is required to maintain the CoH, ring, but I do not consider that each carbon atom can be considered to have an affinity free '

The conclusion here arrived at with regard to benzene, that no direct connexion exists between any but the contiguous carbon atoms in the ring—that para carbon atoms are not and cannot become united—may be regarded as of universal application. Von Baeyer's experiments prove, moreover, that the dihydro tereph thalic acid in which an atom of hydrogen is associated with each of the para-carbon atoms to which the carboxyls are attached, unlike terephthalic acid, behaves as an unsaturated compound, forming a tetrabromide, and that it is to

be represented by the formula $H CO_2H$

this it follows that the type changes on conversion of the 'centric' compound into the di addition compound, and probably this is generally the case, for example, when quinol is converted into quinome. OH O

OH O Quinole.

It would also follow that in the case of benzenoid corpounds four of the six 'spare' affinities can not act 'centrically' To what extent this is true in the case of other rings remains to be ascer tained, from the remarkable similarity of thiophene and benzene, it would appear probable that the former is to be represented as analogous to HC — CH

benzene in structure, thus HC CH, whereas

the analogous compounds furfuran and pyrrole more nearly resemble the unsaturated compounds in their behaviour, but this is perhaps ascribable to the influence exercised by the oxygen or imidogen

The foregoing brief discussion will suffice to direct attention to the numerous problem i comprised in the philosophy of isomerism, and to show how far from final are the conclusions as to structure which we are at present able to arrive at

In a large and rapidly increasing number of instances, it is impossible to assign different rational formulæ to compounds undoubtedly different so long as the system employed takes into account merely the nature of the radicles and the manner in which they are associated as pictured by disposing them in a single plane If, while assuming the hydrogen atoms in a compound, such as methane-in other words the four valencies of the carbon atom-to be equal, it be supposed that the radicles intro duced in place of the hydrogen atoms occupy relatively different positions in the plane, a variety of isomeric derivatives would appear to be possible eg two of the form CRRR, R,, two of the form CRRR, R2, and three of the form CRR₁R₂R₃, R, R₁, R₂, R₃ being different radicles A special study of methane derivatives from this point of view has been made by Henry, but both his results and our general experience show that isomerides such as are here contem plated do not occur

By considering the arrangement of the atoms in space, conclusions have, however, been arrived at which are far more in harmony with experience. Such a step was first taken in 1874 by Van't Hoff (La Chimie dans l'Espace, Rot terdam, 1875), and independently and almost simultaneously by LeBel (Bl [2] 22, 337, cf ibid 23, 295). A German adaptation of Van't Hoff's pamphlet entitled, Die Lagerung der Atome im Raume, was published in 1877 by Hermann A full account of the subject is to be found in the previous edition of this dictionary and in Miller's 'Chemistry,' vol in

The fundamental hypothesis of the Van't Hoff system consists, as is well known, in supposing that the carbon atom occupies the centre of a tetrahedron and that its four affinities are directed towards the four solid angles. When four different radicles are associated with the carbon atom, but only in such a case, two isomerides are possible, represented by two irregular non-superposable tetrahedra bearing to each other the relation of an object to its reflected image, and, moreover, these isomerides should be of enantomorphous crystalline form, as

well as optically active and possessed of erual! and opposite rotatory powers, as the molecules are unsymmetrical, such tetrahedra exhibiting, in relation to an axis drawn parallel to the corresponding edges, a screw shaped grouping of the four summits, turning to the right in the one form and to the left in the other A carbon atom thus situated is termed asymmetric, and is represented in a formula by an italicised C The hypothesis serves therefore at once to ex plain both the existence of isomerides which cannot be represented by formulæ written in a single plane, and to account for the optical activity of certain substances Thus in the case of tartaric acid, which contains two asymmetric carbon atoms, but is composed of two equal groups, (COOH)(HO)HC CH(OH)(COOH), the hypothesis indicates the existence of two opti cally active isomerides of equal but opposite rotatory powers, and a third inactive isomeride in which the optical effect of the one asymmetric carbon atom is balanced and neutralised by the equal opposite effect of the other, it thus accounts for the existence of dextro-, lavo . and meso tartaric acids, racemic acid, the fourth modification, apparently, is to be regarded as a 'physical' allotrope formed by the conjunction of the two active isomerides it would seem that it does not exist in solution Van't Hoff has shown, in a recent much extended new edi tion of his pamphlet, that every prevision of the hypothesis with reference to the optical characters of isomerides has been fulfilled in the most complete manner possible by the in vestigations carried out in the interval since its enunciation by Le Bel and himself (cf Dix Années dans l'Histoire d'une Théorie, Botter dam, P M Bazendijk, 1887), this remarkable agreement of practice with theory has naturally led to the almost universal adoption of the hypothesis

The hypothesis also provides for a greater number of isomerides in the case of compounds of the ethylenic type than is indicated if the space relationship of the radicles be omitted from consideration, if a compound of the form R,R,C CR,R, be represented by two tetrahedra joined so as to have one edge in common, it will be found that only one such figure can be constructed, if either the four radicles are iden tical, or if only R, differs from R, or R, from R,, but if R, is different from R, and R, is also different from R., although R, and R., R, and R., are identical, two such figures may be constructed -this is more readily rendered obvious by the adoption of the simpler plan of writing the symbols of the radicles attached to the two doubly linked carbon atoms on either side of a line representing the plane of their conjunction

Thus the symbols $\frac{a}{a}\frac{b}{b}$ and $\frac{a}{b}\frac{b}{a}$ represent modifi-

cations in which in the one case the two similar radicles are situated symmetrically with reference to a plane at right angles to the axis of the system, and in the other are symmetrically situated with reference to the axis of the system, such modifications may therefore be termed, as Wishicenus has suggested, the plane and axially symmetric modifications. The isomerism of maleic and fumeric acids is regarded by Van's

Hoff as dependent on such a difference in struc-

Such a stereometric mode of formulation does not afford an increased number of expressions for acetylenic derivatives, the same is true of ben-enoid compounds if Kekulé's symbol be adopted (cf Marsh, P M Nov 1888, p 426) It may be noted, however, that the asymmetric carbon atom hypothesis is applicable to the explanation of the optical activity manifested by a variety of closed chain compounds, such as quercitol and quinic acid, which are derivatives of hexamethylene, and conine and its homologues, which are derivatives of piperdine

Although the Van't Hoff Le Bel hypothesis has been very generally accepted as affording a sufficient explanation of a very large number of cases of isomerism difficult to account for in accordance with the existing canons of belief, it is as yet by no means certain that it can be always so regarded, in many cases the difference between isomerides is so great that it is somewhat difficult to believe that it depends on so comparatively simple a difference in structure as the presence of one or more asymmetric carbon atoms would involve The two isomeric tartaric acids are the veritable image the one of the other, but this is rarely the case thus hydrobenzoin differs very considerably from isohydrobenzoin, as do also mannitol and dulcitol. and to a still greater extent the acids, sacchario and mucic, formed from these latter, in all these cases the isomerism is assumed to depend on mere geometrical differences In the case of mesotartaric acid, the intra-molecular neutralisation of one asymmetric carbon atom by the other already produces a marked effect, as evidenced by the difference in properties of this acid in comparison with either of the active modifications It may be, therefore, that in the case of mannitol and dulcitol, and the acids formed by their oxidation, the accumulated effect of the several asymmetric carbon atoms is much greater than in the case of tartaric acid, and hence the greater difference in properties between the iso-Very little alteration is involved in the formation of racemic acid, and, as above pointed out, this substance appears to be a mere physical' allotrope, hardly a polymeride, of its active constituents, in certain cases the formation of the 'racemic form' is attended with a considerable alteration in properties-in the case of leucine and of camphoric acid, for example, their racemic forms being much less soluble and of higher melting points than their optically active constituents In these cases there would seem to be a more intimate union than in the case of racemic acid, the marked difference between saccharic and mucic acid may be due to some such cause as this But the isomerism of the hydrobenzoins is more difficult to explain, assuming that they are both compounds of the formula (C,H,)(HO)HC CCH(OH)(C,H,) Including a racemic form, four modifications of such a compound appear possible, two of which should be optically active Neither compound is optically active, and, judging from Zincke a observations, it does not appear probable that, if the one be the meso or mactive modification corresponding to mesotartaric acid, the other is the racemic form. The assumption that the one, perhaps 86 ISOMERISM.

isohydrobenzoin, contains the two hydroxylgroups attached to the one carbon atom, thus C.H.,H.C C(OH), C.H., would satisfactorily account for its behaviour, but has hitherto been rejected as improbable owing to the general belief that compounds of such a character are exces sively unstable But it may be that the presence of the negative phenyl groups confers stability in such a case, much as in the case of chloral hy drate, and it is well to remember that in not a few instances of late years proof has been given of the incorrectness of views based on general considerations, as in the case of phthalic chlor ide, for example, and the hydroxamic acids

Still greater difficulties occur in accepting the conclusion that the Van't Hoff hypothesis affords an explanation of the isomerism of unsaturated compounds such as maleic and fumaric acids, which, according to this view, are respectively the plane symmetric and axially symmetric isomerides of the formula

HOOC CH HC COOH and нё соон HC COOH Fumaric acid. Maleic acid

It is well known how great are the differences between these two acids, both in physical pro perties and in general chemical behaviour, and that maleic acid alone yields a corresponding anhydride, fumaric acid being converted into the same anhydride when dehydrated Ostwald also has shown that the electrical conductivity of their solutions is such as to indicate that maleic acid is a weak acid akin to selenious and phos phorous acids, whereas fumaric acid is a wellmarked dibasic acid (J pr 32, 362) acid has also a considerably greater heat of combustion than fumaric acid (Thomsen, J pr 40, 202) Roser has suggested that, whereas fumaric acid is a normal di carboxylic acid, maleic acid is to be represented by the formula

HC CO

|| >0 HC C(OH)₂ This formula would afford a satisfactory ex planation of the great differences observed be tween the two acids, and it has been strongly advocated by Anschütz (A 254, 168) No valid argument has yet been advanced which would prevent its adoption

It may here be pointed out that no attention is paid in applying the Van't Hoff hypothesis to unsaturated compounds to the peculiarities which are manifest in such compounds, and which ap parently must be attributed to the presence of unsaturated carbon atoms, a 'double or ethylenic bond' is represented as the precise equivalent of two single bonds, and a 'treble or acetylenic bond' as the equivalent of three single bonds, which is certainly not in accordance with facts, and especially with Thomsen's observations on the heats of combustion of unsaturated compounds

Wislicenus has not only accepted the Van't Hoff Le Bel hypothesis in its entirety, but has in the most ingenious manner possible extended its application, and has endeavoured both to elucidate the structure of geometrically isomeric unsaturated compounds, and to explain the '150meric changes 'which such compounds frequently exhibit (Abhandlungen der math. phys. Classe

der könig Sächsischen Ges der Wissenschaften, Band xiv Leipzig, 1887).

In the case of maleic and fumaric acidassuming that these are stereometric isomeridesas pointed out originally by Van't Hoff, the for-HOOC CH

may without hesitation be mula HC COOH

assigned to the latter, as it is incapable of form ing an anhydride, whereas maleic acid, being easily convertible into the anhydride, is repre нс соон

sented by the formula in the case нс соон '

of crotonic and isocrotonic acids however, it is more difficult to find criteria on which to base a choice between the formulæ

HC CH, CH, CH and HC COOH HC COOH

and similarly in other cases Wislicenus con that if a compound of the form $C_1R_1R_2R_3R_4$, consisting of the two systems $R_1R_2C_3$, and $C_1R_3R_4$, be derivable from a cor responding acetylenic compound, its constitu tion can at once be inferred from the fact that when one pair of bonds between the carbon atoms in the acetylenic compound is severed, as the two atoms are still united by double bonds. no rotation of the systems can take place, consequently the added radicles both occupy posi tions on one side of the common axis of the Thus the tolane dichloride melting at systems 143°, obtained by chlorinating tolane, is neces sarily the plane symmetric modification

C.H.C C.H. CCI Ш C,H,C C,H, CCl

The isomeride of lower melting point (63°) must therefore be regarded as the axially symmetric

C.H. CCl compound In principle this CIC C,H,

method appears perfectly sound, but it is based on an assumption with reference to the manner in which the carbon atoms in ethylenic and acetyl enic compounds are united, which, as previously pointed out, is perhaps open to question, it also involves the conclusion that the radicles attached to the carbon atoms are incapable of changing their positions, which is also by no means a safe assumption, bearing in mind the extreme readi ness with which 'isomeric changes' occur

A method of more universal application, but involving much more complex considerations, is the following In saturated compounds in which the carbon atoms are united by single affinities. one carbon system must be capable of rotating about another, moreover, it is to be assumed that the atoms in a molecule—even those which are not directly connected—exercise an influence on each other, and will therefore tend to condi tion such rotation so that radicles which have the greatest affinity are brought into the closest proximity possible Thus, on converting ethyl ene into its chloride, in the first instance the change would take place in accordance with the following scheme

But, in consequence of the superior affinity of hydrogen for chlorine, such a system would be unstable, rotation would set in, and the more CHHCl

stable system

| would result.

To take another case, that of the conversion of tolane tetrachloride into dichloride by reduction, this compound may present three configurations, viz

CC,H,ClCl CC,H,ClCl CC,H,ClCl

It would probably chiefly consist, especially at low temperatures, of the second and third modifications, as the dissimilar radicles are most proximately situated in these, and as these two modifications would both farnish the axially symmetric dichloride on reduction, it is to be supposed that the chief product of reduction will be this dichloride, actually that melting at 63° is chiefly obtained (Blank, A 248, 1), and it is, therefore, to be supposed that this modification is avially symmetric—a conclusion which harmonises with that previously arrived To this it may be objected that our know ledge of the relative affinities of the radicles within a compound is purely hypothetical, and that it is by no means certain that dissimilar radicles would in all cases tend to influence and attract each other more than would similar ra-Thomsen's observations on the heats of combustion of chlorine compounds, in fact, would appear to favour an opposite conclusion more important argument is to be found in the fact that in cases in which the constitution may fairly be regarded as established, the relation is of the obverse order to that required if the con tention of Wishcenus be correct thus, the sym metric or para diderivative of benzene always has the highest melting point, the same appears to be true of the symmetric tri and tetra-deri vatives, and, in the case of naphthalene, the axially symmetric isomeride is always that of highest melting point (cf. C. S. Proc. 1888-93)

Another use which Wish cenus has made of the

Another use which Wishcenus has made of the argument here criticised may now be mentioned. It is a well known fact that maleic acid is very readily converted into fumario by the action of acids. Wishcenus supposes that when this con version is effected for example, by bromhydric acid, the double bond becomes severed, bromosuccinic acid being formed.

HC COOH HC COOH + HBr = HCH COOH HCBr COOH

but rotation setting in, the radicles are brought into their preferential positions, viz HOOC CHH

HC BrCOOH, and when, by the action of the water present, this modification becomes deprived of hydrogen bromide, fumaric acid naturally results. Although in the highest degree in agenious, this conception unfortunately does not appear to be in accordance with the facts, for, as Anschutz points out (2. 254, 168), the conversion takes place under conditions under which the succinic derivative is stable, and there is no reason therefore to suppose that such a compound is formed at any stage of the conversion of maleic into fumaric acid, if maleic acid be formulated in the manner advocated by An-

schutz, its conversion into fumaric acid by acids is easily understood

Victor Meyer's researches have led him to carry speculation even further On submitting benzil to the action of hydroxylamine, Meyer and Goldschmidt obtained an a dihydroxime which they found was converted into a more stable &isomeride by heating with alcohol to about 180° a careful investigation of these compounds was subsequently made by Meyer and Auwers, but they were unable to discover any substantial difference in their chemical behaviour, and they came to the conclusion that both must be regarded as compounds of one and the same formula C.H. C(NOH) C(NOH) C.H. As the existence of two such compounds was incompatible with the assumption that carbon atoms united by single affinities are free to rotate, Meyer and Riecke (B. 21, 946) have put forward an hypothesis as to the nature of the carbon atom itself which serves to account for two kinds of union by single affinities, one in which rotation is impossible, the other in which it can freely take Having regard, however, to the readiness with which 'isomeric change' takes place. and to the extremely imperfect state of our knowledge of the exact manner in which polyad ele ments are held in association, there cannot be any doubt that it is premature to conclude that the benzil dihydroximes are necessarily structurally identical, the study of chemical inter-changes is after all but an approximate and fallible mode of determining structure

Hantzsch and Werner (Ber 23, 11) have quite recently proposed to extend the Van't Hoff conception to the introgen atom itself. They suppose that in some nitrogen compounds the three affinities of the nitrogen atom are directed towards three of the solid angles of an irregular tetrahedron, and that the nitrogen atom itself is located at the fourth. In the case of compounds of the form CXY NZ, which are comparable with carbon compounds of the form CXY CHZ, it is conceivable that the Z radicle may alter its position in space relatively to the radicles X and Y and thus give rise to isomerides

Victor Meyer (B 23,567) has, however, pointed out that the views of Hantzsch and Werner are in many respects in conflict with the experimental evidence. This memor is a noteworthy contribution to the discussion of a number of the more obscure cases of isomerism. (The two papers here referred to have been published since this article was in type)

It is here the place to refer to the numerous discussions which have taken place during late years in cases in which one set of interactions of a compound appear to be in accordance with one formula, while another set favour a different but closely related formula, which have led, in fact, to the recognition of labile or pseudo-forms capable of passing spontaneously into stable forms For example, it has long been a question whether ethylic acetoacetate is to be represented as CH, CO CH, CO, Et or by the formula CH, C(OH) CH CO,Et A discussion of such cases has been given by Laar (B 18, 648, 19, 380), who proposes to term such isomerides But, as he practically himself tautomeric. admits, the use of such a term savours of tauto88 ISOMERISM

logy. V. Meyer subsequently brought forward a suggestion of Jacobson's to substitute desmotropic for tautomeric Hantzsch and Herrmann (B 20, 2801), while using the term tautomerism when speaking of compounds capable of passing from the one type into the other, proposed to limit the term desmotropic to each of the states As the phenomena in question are the outcome of mobility and not of fixity, the new term also appears to be particularly ill chosen, and bearing in mind the intention of Berzelius in introducing the term metameric (see p 81), it would appear that this old term is a peculiarly appropriate one to use in such cases Laar suggests that a compound which is capa ble of an 'alternative' behaviour actually has an alternating structure, the intra-molecular condition being such that the structure is of one kind at one moment and different at another But, as Hantzsch and Herrmann remark, it is scarcely necessary to make such an assumption Ethylic succinylosuccinate and its derivatives manifest the peculiarity in question in a high degree, acting sometimes as quinonic compounds and sometimes as quinols, s.e in modes such as correspond to the presence of one or other of the two forms CO CH(CO,Et) and C(OH) C(CO,Et) As a rule only one of the forms is stable, the other being developed in the course of the change, thus phloroglucol appears to be a true trahydroxylbenzene, 2 e a phenol, but frequently it affords derivatives of 'triketohexamethylene, which may with propriety be termed phloroglucone Thus

It is not improbable that in those cases in which the several forms can be obtained in a definite crystalline form, the necessary stability is conferred by union of the fundamental molecules amongst themselves. The formation of such molecular complexes is rendered probable by a large number of observations, one of the most striking is that recently brought forward by Perkin in the case of orthomethoxybenzalde hyde CH₂O C₂H₄ COH (C J Trans 1889 549), which is capable of existing in two solid modifications, one unstable melting at 3°, the other stable and melting at 35 5° A list of similar cases of what is sometimes termed physical isomerom is quoted by Perkin

Having thus briefly touched on the numerous problems which the study of the different kinds of allotropism presents, it appears desirable finally to re-direct attention to the terminology of the subject.

The term allotropic, as already pointed out, has a perfectly general meaning and is therefore applicable to the phenomena generally, and may be used in all cases in which the nature of the relationship is obscure

According to our modern conceptions, truly isomeric substances—substances composed of equal parts—are equi-molecular compounds containing identical radicles arranged in relatively

different modes, and on the principle of calling a spade a spade, bearing in mind that it was obviously the intention of Berzelius to limit the scope of the expression, the term isomeric should be used only with reference to such compounds The space relationship of the radicles being the determining cause of isomerism, although it is not always requisite in order that it may become apparent to express their relationship according to stereometric canons, it is scarcely necessary to make any principal distinction between cases, such, for example, as occur among benzene derivatives and between the tartaile acids, but if it be thought desirable to call attention in some way to the finer isomerism which obtains in cases such as the latter, the term erkorsomerism, from εἰκών, a likeness or image, may be suggested as not mappropriate

Typically different allotropes belonging to different classes of compounds might well be termed heteromeric, metameric being reserved for those heteromeric allotropes which change their type with exceptional facility in the course of chemical interchanges, but if the use of the term in this restricted sense be objected to, such allotropes might advantageously be spoken of as isodynamic Allotropes belong ing to the same class but consisting of different radicles-the butylic alcohols, for examplemight be to med isonomic It appears unnecessary to specially distinguish the physical iso merism manifest in the occurrence of several crystalline forms of different melting point. The phenomena of pleomorphism generally, as well as those involved in change of state from solid to liquid and gas, and the existence of allotropic forms both of the metallic and nonmetallic elements, are now being more and more generally attributed to changes in molecular complexity, and if this be the case, such allo tropes mostly partake of the nature of polymeric allotropes

ISOMORPHISM (loos, equal to, μορφή, form) In the year 1819 Mitscherlich (A Ch [2] 14 172) discovered that certain arsenates phosphates of analogous constitution crystallised in the same form, subsequent investigation (A Ch [2] 19, 350, 24, 264, 355) led to the general conclusion that substances of analogous chemical constitution possess the same or nearly the same crystalline forms, and will under suitable conditions crystallise together in all proportions to form homogeneous mixed crystals. such substances are termed isomorphous spite of numerous attempts to widen or otherwise modify it, this definition has lasted to the present time Owing, however, to recent researches, especially those of Groth, it will be best not to treat isomorphism as an isolated phenomenon, but as a part of that branch of physical chemistry which studies the relations between the chemical compos tion and crystal line form of bodies, and which from a knowledge of the constitution and chemical properties of a substance seeks to pred ct its system, form, and crystallographic constants. We are still very far indeed from doing anything approaching to this, for, although attempts have not been want ing -v Schrauf (Physikalische Mineralogie, 1868 bd 2, 166, Z K 9, 265) and Barlow (O N 53, 3, 16) - small success has so far attended them, and at present crystal form cannot be deduced from a knowledge of chemical constitution and properties alone, if, however, we find that in a given case certain atoms arranged in a certain definite way are accompanied by a certain definite form, we may argue that similar atoms similarly arranged will be accompanied by a similar form This hypothesis is found to be true, and its verification has resulted in the dis covery of relations between the forms of substances more or less chemically allied relations may be conveniently discussed under the three following heads

I The same chemical substance possesses two or more forms-Polymorphism

II Bodies more or less closely related chemically have more or less analogous forms-Morphotropy, including Isomorphism

III Bodies not chemically related possess the same form -Isogonism

Full references, especially for the early history of the subject, will be found in the article Isomorphie by Argruni, in Fehling's Handworterbuch der Chemie, 1878 vol 3, for more recent work Fock's Entetting in die Chemische Crystallographie, Leipzig 1888, may be consulted, while full lists of substances considered isomorphous have been given by Topsoc, Tiditrift for Physik of Chemi, 8, 5 193, 321, 9, 225 summarised by Arsruni above For the use of isomorphism in determining atomic weights r ATOMIC AND MOLECULAR WEIGHTM, vol. 1, p 335

POLYMORPHISM Haüy believed that every substance possessed its own characteristic form, and, in spite of numerous observations tending to establish the chemical identity of calcite and arragonite (v De Lisle, Klapproth, Thenard, and Stromeyer), refused to admit that the same substance could yield two distinct kinds of crys tals In the course of the work on the arsenates and phosphates which led him to announce that two different chemical compounds could possess the same or nearly the same crystalline form, Mitscherlich found that NaH2PO, H2O gave, ac cording to the conditions, two kinds of crystals, while his discovery in 1823 (A Ch [2] 24 264) that sulphur crystallised both in rhombic and oblique forms readily convertible the one into the other by change of temperature alone, esta blished conclusively that the same substance could exist in two different forms, to express these phenomena Mitscherlich proposed the term dimorphism, and in 1828 recognised the possibility of trimorphism. The existence of several modifications of the same substance may be generally expressed by the terms polymor phism or heteromorphism At the present time these terms are usually applied to compounds only, polymorphism, when exhibited by elements, being termed allotropy (q v, vol 1 p 128) The change of one dimorphous modification into another has been especially studied by Lehmann, and all known cases have been collected and dis cussed by him in his Molekularphysik, 2 vols Leipzig, 1888 (vol. 1 pp 119-219, vol 11 pp 898-415)

MORPHOTROPY From the time of Mitscherhch onwards the rap.d growth of organic chemistry provided a large number of new sub stances for crystallographic examination, and as the existence of many cases of isomorphism among inorganic substances had been esta blished, numerous attempts were made to introduce the same conception into organic chemistry

In general, however, these efforts were fruitless, and the researches merely resulted in the introduction of new terms and in several attempts at widening Mitscherlich's definition

Thus Laurent, who investigated the halogen substitution and addition products of naphthalene and salts of the fatty acids, concluded that identity of system is not necessary for isomorphism. Nicklés and De la Provostaye collected cases of analogous angles and introduced new terms, such as hemi isomorphism, isomeromorphism, and hemimorphism, to express those cases in which crystals of two substances had each a zone with nearly similar angles (v papers by these authors, C R 11, 15, 20, 23, 26, 27, 29) Pasteur again (C R 26, 535) found analogies between the tartrates, while other workers in the same direction were Rammelsberg, Marignac, Delafosse, Sella, and Hjortdahl (J pr 94, 286) Owing to the paucity of results, such researches lost favour till Groth, in 1871 (P 141, 131, B 3, 449), attacked the subject from a new point of view, and set himself to investigate the changes in crystal form which take place when one or more of the hydrogen atoms of an organic molecule, such as benzene, are substituted by other atoms or groups relations observed between the form of the parent substance and the form of the substituted body Groth terms morphotropic relations, while he attributes the actual change of form produced by substitution to the morphotropic force of the elementary atom or group Benzene, which crystallises in rhombic pyramids, was the first substance examined by Groth, he compared its form with the forms of as many as possible of its hydroxy-, nitro, amido, and haloid, substitution products, and his researches have led to the following general statement. The less the chemical character of the combination is changed by substitution the less is also the change of crystal form, which depends

1 On the specific morphotropic properties

of the substituting atom or group,

2 On the chemical nature and crystalline system of the body in which substitution occurs, 3 On the relative positions of the substituting

atoms or groups in the molecule

1 Morphotropic properties of atoms and groups

(a) The metals Potassium and ammonium, when substituted for H, only change one axis, thus -

rhombic 0 937 1 Picric acid 0 942 1 352 Potassium picrate

As a rule, all the alkalı metals produce the same

(b) Substitution of OH for H in benzene derivatives only alters the crystalline form slightly, and in rhombic substances the ratios of two of the axes remain unaltered, and only the third axis is materially affected

NO, and NH, behave much like OH

				a	ь	c
Benzene			rhombic	0 891	1	0 799
Resorcin			11	0 910	1	0 540
Nitrophenol	12	-	"	0 878	1	0 600?
Dinitropheno	l 1	24	**	0 933	1	0 758
Truntrophen				0 987	1	0-974

(c) Cl, Br, and I act more energetically, but less regularly, than NO₂. The angles of one zone, however, remain like those of the parent substance, while the system is generally altered to one of lower symmetry

Benzene rhombic 110 $1\overline{10} = 96^{\circ}$ 30' Dichlorobenzene oblique ,, , 98° 40' Tetrachlorobenzene ,, , 96° 17'

(d) The influence of the CH₃ group is extremely variable, depending very much on the nature of the substance into which it enters Among the substituted ammonias it is often without influence, thus, 2NH₄Cl PtCl₄, 2NH₄Cl PtCl₄, 2NH₄Cl PtCl₄, all crys

tallise in the cubic system

2 Influence of the nature of the When the parent sub parent substance stance belongs to the cubic system, substitution has either no influence on the form, or else causes change to a system of lower symmetry In other systems the axial ratios may alone alter, or the system itself may be changed, according to the morphotropic force of the substituting element or group If the hydrogen atoms of like functions are replaced singly the system fre quently at first changes to one of lower symmetry, but when the substitution is complete returns to the symmetry of the parent substance methyl substitution compounds of 2NH,Cl PtCl, illustrate this well

2NH₄Cl PtCl₄ Cubic 2NH₃(CH₃)Cl PtCl₄ Rhombohedral 2NH₂(CH₃)₂Cl PtCl₄ Rhombic 2N(CH₃)₃Cl PtCl₄ Cubic 2N(CH₃)₄Cl PtCl₄ Cubic

As an illustration of the influence of the chemical nature of the parent substance, we may quote the observation of Hintze that, contrary to the general rule, the substitution of the paraffinoid H in (C_bH_j)₅CH by (OH) or Br raises the symmetry, instead of lowering it

3 Influence of position—The relative position of the substituting atoms in the mole cule has a very great influence on the form of the crystal, but we are very far from being able to connect form and constitution

As a rule the crystals of isomerides exhibit very few analogies, and in many cases none at all In the benzene series, however, a few relations have been observed, though even here they are rare, and often more readily detected by a comparison of the isomerides with the parent sub stance than directly with each other. Thus a comparison of the angles given by Bodewig (P 158, 232) for the three dinitrobenzenes shows that certain analogies do exist, although the compounds do not crystallise in the same system, while meta $C_8H_4(NO_2)_2$ is related to benzene itself, as is shown in the following table.

The above examples suffice to show vary clearly that the great influence exercised by position renders the discovery of the morpho tropic properties of an element or group very difficult. Thus we have stated above that the entry of the nitro- group into benzene leaves the

system and axial ratio a b unaltered, while the c axis is more or less changed This statement for o C₀H₁(NO₂)OH, C₀H₂(NO₂)₃OH(1 2 4 6), we found held good for C₆H₃(NO₂),OH(1 2 4), and $m \, C_e H_1(NO_2)_2$ As soon, however, as we become acquainted with o and $p \, C_e H_1(NO_2)_2$ the generality of our statement disappears, and the exact morphotropic value of the NO, group remains still undetermined Although we are not in a position to deduce form from a knowledge of constitution alone, we may often from the chemical analogy of two substances, the form of one of which is known, draw conclusions as to the form of the other, or, vice versa, knowing the form of two substances, and the constitution of one of them, we may draw conclusions as to the constitution of the other This method has been chiefly employed in inorganic chemistry, but Friedlander (Z K 3 168) has made use of it in order to throw light on the constitution of the tri nitrobenzene got by nitrating $m C_6H_1(NO_2)_2$ The trinitrobenzene made in this way may be either of three theoretically possible ones It crystal lises, however, in the rhombic system, and has the axial ratios 0 954 1 0 733, and agrees ac cordingly with m C₆H₄(NO₂), On the other hand it shows little or no analogy to the forms of o or p C₆H₄(NO₂)₂, and it is therefore probable that this substance is symmetrical trinitrobenzene 135 A comparison of its form with that of acid $C_6H_2(NO_2)_8OH(1356)$, rhombic pierie 0 937 1 0 974, confirms this view

ISOMORPHOTROPY and ISOMORPHISM When the products obtained by replacing the hydrogen atoms of the parent substance by two closely allied atoms or groups are compared together they are often found to crystallise in identical or nearly identical forms, such products are isomorphous, while the substituting atoms or groups are said to possess the same morphotropic force, or to be isomorphotropic. Thus, K and NH4 are isomorphotropic, and replace the H of

acids to give isomorphous salts

The term morphotropy was first applied to cases in which an atom of H was substituted, but the conception may very conveniently be extended to include all cases of substitution whatever, thus, KBr may be regarded as derived from KCl by substituting Cl by Br, and since KCl and KBr both crystallise in the same system and possess very similar physical characters, they are isomorphous, while Cl and Br are isomor The greater the analogies between photropic the substituting atoms the greater is the corre spondence between the forms of their compounds, ie the more closely isomorphous are they, but because two elements are isomorphotropic when in combination with one set of atoms or groups it does not necessarily follow that they are always isomorphotropic, for the morphotropic force of any atom is largely conditioned by the compounds in which it finds itself Again, Kopp (P 53, 446) has pointed out that although it is often true that two isomorphous substances combine with a third to form two isomorphous compounds (Schröder), we cannot, as has been too frequently done, deduce the isomorphism of elements from the isomorphism of their compounds, there are few elements which cannot by such a mode of reasoning be made isomorphous Elements are only truly isomorphous when they

actually crystallise in the same forms, if they merely combine with another element or group to form isomorphous compounds they may be spoken of as isomorphotropic in that particular class of compounds As we have seen, the conception of morphotropy includes that of isomorphism Now, ever since the latter term was introduced, great difficulties have been felt in defining it. and in finding tests which might authoritatively decide in any given case whether two substances were isomorphous or not Mitscherlich's defini tion is vague, for we at once ask, What constitutes chemical analogy? And again, How widely may the angles of two substances differ and the substances stall be considered isomorphous? The truth seems to be that no hard and fast line can be drawn between those substances which are so closely related morphotropically as to be considered undoubtedly isomorphous, and those slightly less closely related whose isomor phism is doubtful, while we may pass by im perceptible stages from truly isomorphous bodies to others to which, although they still exhibit relations, this term is as evidently inapplicable Although it seems impossible in the present state of our knowledge to give a definition which shall distinctly mark off isomorphous bodies from those which are merely closely related morphotropically, this is not in practice attended with any very great inconvenience, for the difficulty is chiefly one of nomenclature, most cases of isomorphism are at once recognised as such, and it is only in comparatively few instances that we must hesitate

In doubtful cases much assistance may often be obtained by a comparison of the other properties of the two substances. Besides great similarity of form, agreement in several other physical properties has been thought necessary before two substances could be considered iso morphous, and we must now notice in detail the more important of these properties, pointing out the weight which has been attached to each as a test of isomorphism

Physical properties of isomorphous substances

(a) Geometrical properties. As the name itself implies, near equality of external form is the first and most essential condition for iso morphism Absolute geometrical isomorphism, however, does not exist except in the case of sub stances crystallising in the cubic system, in all other systems small differences of angle occur a fact first noticed by Wollaston These differences are seldom equally distributed, in rhombic oblique and triclinic crystals the anomalies are often confined to one zone, another zone per pendicular to the first having the same angles in both cases Here a difficulty meets us, for we ask, How great may these differences become and the substances still remain isomorphous? Unfortunately no definite answer to this question is possible, some authors have admitted much wider differences than others, while others still have gone so far as to admit that the boundaries of the systems may be overstepped It is perhaps best to restrict the term isomorphous to substances crystallising in the same system with nearly the same angles. It is to be noted that though all substances crystallising in the cubic system have exactly the same angles

they are not necessarily isomorphous, to be so they must be either both holohedral or must both possess the same kind of hemihedrism, and must also agree in other properties, such as cleavage and power of forming mixed crystals

(b) Cleavage Isomorphous bodies possess as a rule the same cleavages variations in the relative perfection of such cleavages are, how ever, possible This property is especially useful in assisting us to detect isomorphism in the cubic system

(c) Thermal conductivity Jannetaz (C R 75, 1501) has shown that certain isomorphous substances have axes of maximum and minimum conductivity of like direction and magnitude

(d) Coefficient of expansion The data are not sufficient for general conclusions to be drawn, and no simple relations have been detected at present

(e) Etched figures Since these stand in a close relation to crystalline form, Baumhauer has sought to use them as a test of isomorphism He finds that isomorphous substances give, as a rule, the same sort of etched figures, but that they often differ in orientation

(f) Optical properties These have been specially compared by Senarmont (A Ch [3] 33, 391), Topsoe, and Christiansen (A Ch [5] 1, 5) No general law has been established, but as a rule isomorphous bodies if uniaxial have the same sign of double refraction, and if biaxial have the plane of the optic axes similarly oriented, but biaxial crystals, oblique and triclinic ones especially, exhibit frequent exceptions. Optical properties are, moreover, very sensitive to changes of temperature, which often do not influence isomorphous substances to the same degree (Arzruni, Z K 1, 165)

(g) Specific volume

themical composition, SV, and crystalline form are of special importance, since several authors have considered near equality of SV an essential condition for isomorphism. The first of these was Kopp (A 36, 1, P 47, 133, 52 243, 262, 53, 446), his views may be briefly summarised as follows. (1) The condition for isomorphism is equality or near equality of SV. The answer to the question, how widely may the SV's differ and the substances remain isomorphous, is given by the empirical formula.

 $D = \frac{\iota - \iota_1}{\frac{1}{6}(\iota + \iota_1)}$ where v and ι_1 are the S V 's of the

two substances If D=0 the isomorphism is perfect, but if D is greater than 33 the substances are not isomorphous, thus the value of D for the two substances ZnCO₃ and CaCO₃, whose S V's are 28 2 and 36 8 respectively, is 264, they are, therefore, isomorphous (2) Kopp has also pointed out that the nearer are the axial ratios of a series of isomorphous bodies the nearer are their S V's This statement, though criticised by Schröder, appears to hold good, and has received the support of Tschermak (Sits W 45'[2] 603) and Schrauf (P 134, 417) The former expresses the law as follows 'The series of crystal dimensions and specific volumes is in each group of isomorphous bodies of analogous composition the same' As an illustration he gives the series of rhombohedral carbonates.

	a	đ	
ZnCO,	1	0 807	282?
MgCO.	1	0 812	279
(MgFe)CO.	1	0 814	29 2
FeCO,	1	0 819	30 2
MnCO,	1	0 822	31 9
CaCO	1	0 854	36 8

Schröder (P 50, 553, 95, 441, 562, 106, 226, 107, 113) at first held views much resembling those of Kopp, but in his later papers he comes to the conclusion that the statements made above are erroneous, and expresses himself thus 'The specific volumes of isomorphous compounds differ in general quite as much from one another as the specific volumes of corre sponding heteromorphous compounds' (Schroder uses the term heteromorphous as opposed to isomorphous, it is now often considered synonymous with polymorphous), and he believes that his results lead him to a new law, viz 'If two elements or groups, A and B, enter into combination with other elements or groups c, D, E, &c, to form the compounds A c and B C, A D and B D, A E and B F, &c , belonging to the same type and asomorphous by pairs, then the differences of the specific volumes of A c and B C, A D and B D, A E and B E, are always equal' If, however, the pairs of compounds are not isomorphous, or if the isomorphous pairs belong to different types, the differences are as a rule unequal Schröder terms bodies of equal SV isosteric, and the equality of the differences of analogous pairs parallelosterism Adopting this nomenclature, the above law may be shortly expressed thus 'Isomorphous analogous pairs of like type are also parallelosteric

Tschermak (lc) finds that, although Schröder's criticism of Kopp is unfounded, his own results support Schröder's law, which he enunciates thus 'Among isomorphous bodies a like difference of composition corresponds to a like difference of specific volume, 'thus the difference Br-Cl is about equal to 63

Apparent exceptions to Schröder's law are believed by Tschermak to be due to difference of constitution in the substances compared, and he illustrates this by the following table of difference for the change of composition K to Am

	s v		sv
KCl	37 9	KBr	44 3
A mCl	352	AmBr	422
	27		21
	SV		8 V
K ₂ PtCl ₄	134 5	K ₂ SO ₄	65 6
K ₂ PtCl ₅ Am ₂ PtCl ₅	150 5	Am_2SO_4	74 6
•	160		90

We see from this table that substances of the type M'_2PtCl_e cannot be directly compared with those of the type M'_2SO₄ or these again with M'Cl

Tschermak has, moreover, endeavoured to trace a connection between the varying differences shown by pairs of elements which occur

in compounds of similar constitution, and the crystal-system to which these compounds belong.

Cubic	8 V	Oblique S∇.
Am, PtCl,	150 5	Am ₂ Cu(SÕ ₄) ₂ 6aq 218
K ₂ PtCl ₄	134 5	K ₂ Cu(SO ₄) ₂ 6aq 205
	160	18
Am ₂ IrCl _e K ₂ IrCl _e	156 138 3	Am ₂ Mg(SO ₄), 6aq 209
		K ₂ Mg(SO ₄) ₂ 6aq 196
	17 7	13
Tetragonal		
Am ₂ CuCl ₄ 2aq	137	Am, Fe(SO4)2.6aq 212
K ₂ CuCl ₂ 2aq	133	K ₂ Fe SO ₄) ₂ -6aq 197
	4	15
Rhombic		
Am,SO,	746	Am.Zn(SO4), 6a4 211
K.SO.	65 6	K ₂ Zn(SO ₄), 6aq 201
- '	90	10
	00	10

Thus he finds that for the change of composition Am_2 to K_2 the difference of S V is greatest in the cubic system, less in the oblique, still less in the rhombic, and least in the tetragonal system

In connexion with SV we may note that at or about maximum and minimum points of the atomic olume curve (v Periodic Lin) occur ductile metals crystallising in the cubic system, eg Na, Mg, Al, K, Fe, Co, Ni, Cu, Pd, Ag, Pt, Ir, Au, Hg, Pb

Although isomorphism is usually accompanied by similar values for the SV's, we cannot from the near equality of SV alone deduce the isomorphism of two substances, neither can we at the present time attachmuch weight to Kopp's empirical formula as a test of isomorphism, in a general way, however, his results, in common with those of Tschermak, Schröder, and Schrauf appear to hold good, owing, however, to the great discrepancies which exist between the relative densities of many of the commonest substances as given by different observers, we must be cautious in accepting conclusions often resting on doubtful data

Special properties of isomorphous substances

- (a) Formation of layer crytals
- (b) Formation of mixed crystals
- (a) Layer crystals These are made by growing a crystal of one substance in a solution of another

Kopp (B 15, 1653) considers regular growth under these circumstances the best test of iso morphism

Thus a crystal of common alum when brought into a solution of chrome alum continues to increase regularly, again the sulphates of the type M"SO, 7aq where M" = Zn, Mg, Fe, Co, Ni, grow in solutions of one another

In those cases where the forms of the two substances are the same the new particles have exactly the same orie tation as those of the nucleus Klocke (Z K 2, 144) has, however, brought to light differences between the phenomena of growth in such cases, and in those where a crystal grows in its own solution Having produced etched figures on the faces of two potassium alum crystals, he grew one in its

own solution, the other in a solution of an monia iron alum, in the first case the etched figures were rapidly filled up from the bottom, in the second very much flattened octahedra of ammonia iron alum were developed at certain points on the crystal of common alum, and perfectly parallel to it, they then increased laterally, and covered up the etched figures, which remained unaltered till the new layer reached them

Although the power or forming overgrowths seems to be a mecessary consequence of isomorphism, the property is not confined to isomorphous substances alone, and from the perfect conformity of form and orientation exhibited by isomorphous substances, such as the alums, we may pass by imperceptible stages to cases of regular orientation among substances possessing but little chemical analogy and crystallising in differer. systems Thus rutile TiO₂, tetragonal, is often found developed on the basal plane of hæmatite Fe₂O₂, rhombohedral, in such a way that the c axis of the rutile lies in a plane of symmetry of the hæmatite

A specially interesting and much discussed case of overgrowth is that of calcite CaCO, rhom bohedral rr' = 74° 55' and Na \ O₂ rhombohedral rr' = 73° 27' When a rhombohedron of CaCO₄ is placed in a solution of NaNO, this substance is deposited on the former in small rhombo hedra, whose morphological axis and planes of symmetry are exactly parallel to those of the CaCO_s, these rhombohedra grow till they meet, a polysynthetic crystal being the result accordingly made a difference between growth in this case and the regular increase of alum crystals, in the light of Klocke's work, and taking into consideration the slight difference of the angles rr', such a distinction vanishes, and if the formation of overgrowths is a test of iso morphism, these two substances are certainly isomorphous, a view confirmed by the agree ment in their other physical characters, the dif ference in their chemical constitution leads us rather to regard them as an example of isogonism.

Closely connected with the formation of layer crystals are Thomson's researches on super saturated solutions (C J 1879 196), he has shown that supersaturated solutions of certain salts can readily be crystallised by the addition of crystals of isomorphous salts, while crystals of substances not possessing the same form, or fragments of amorphous bodies, such as glass, have no influence Thus a supersaturated solu tion of MgSO, 7aq is at once crystallised by ZnSO, 7aq, NiSO, 7aq, and also by CoSO, 7aq and FeSO, 7aq, whose action, however, is less rapid, on the other hand, Na₂SO₄ 10aq, NaCl, and glass, are quite mactive Common alum can be crystallised by iron and chrome alums, while other cubic substances, such as NaCl, FeS, and Fe₂O₄, are mactive

This appears to be an excellent test of isomorphism as far as it goes, but it unfortunately is of very limited application

Although at the present time the formation of layer-crystals cannot be considered a conclusive proof of isomorphism, the success or failure of attempts to obtain them may help us to determine whether two substances crystallising in the cubic system are isomorphous or not.

(A discussion of numerous cases of layer-crystallisation will be found in Lehmann's Molekularphysik, Bd 1 pp 393-407, v also Wackernagel, Kästners Archiv, 5, 293, and especially Kopp, B 12, 901)

(b) Mixed crystals To obtain mixed crystals rolutions of two substances are mixed, or in some cases the two substances are simply melted together, and then allowed to crystallise, we thus obtain perfectly homogeneous crystals, which do not, however, contain their components in any fixed ratio

As a rule only isomorphous substances yield mixed crystals, and their formation is usually considered the best criterion of isomorphism [Klein (C R 95, 781), Kopp (B 12, 868, 17, 105), but v also Brugelmann (B 17, 2359), and especially Lehmann (l c Bd 1 420, 456, 461)]

Numerous researches have been undertaken with a view to the elucidation of the constitution and mode of formation of mixed crystals, while other investigators have endeavoured to trace the connexion between their physical properties and those of their components

Growth of mixed crystals Mixed crystals are most readily formed when the two substances have nearly equal solubility, and in this case Rammelsberg (P 91, 321) has found that the ratio of the two salts in the mixed crystal is about the same as in the solution, mixed crystals of ZnSO, 7aq and MgSO, 7aq afford a case in point, if, however, as more usually happens, the solubilities differ, the first crystals always contain most of the less soluble salt, the last most of the more soluble, such salts are CuSO, 5aq and MnSO, 5aq Thomson (lc) has pointed out that in the case of the crystallisation of supersaturated solutions consisting of a mixture of two substances, the composition of the mixed crystal depends very much on the velocity of crystallisation, if this takes place suddenly the composition of the mixed crystal is much the same as that of the solution, if slowly the less soluble salt is deposited first

The physical properties of mixed crystals

(a) Geometrical properties Mixed crystals belong to the same system as their components, but exhibit simpler forms, cf calcite and dolomite, and v also Rammelsberg (lc) In some cases the angles of mixed crystals lie between those of their components, this usually holds good for the naturally occurring mixtures of the rhombohedral carbonates, thus

Chalybite FeCO₃ rr' = 72° 59' Pistomesite (FeMg)CO₃ = 72° 42' Magnesite MgCO₃ = 72° 32'

But even in this series exceptions are not wanting, and as a rule no simple relation can be detected between the angles of the mixed crystals and those of its components, thus Groth (P 133, 193) in the case of the permanganates and perchlorates found that the angles of the mixed crystals often lay outside those of their components.

In the crystal containing 1Mn 1/Cl the ratio b c lies inside the limits, and the other two outside, further increase in the quantity of Mn causes the form of the mixed crystal to approach nearer to that of KClO. Similar results have been obtained by Arzumi on the alkaline earths (B 5 1043), Meminar on baryto collectin (Min Met 1875 59), v Lang on Am₂SO₄ and K₂SO₄ (Sitz W 1858 31, 85), Arzumi and Baerwald on compounds of FeS₂ and FeAs₂ (Z K 7, 337), and lastly by Miers in his investigations of proustite and pyrargyrite (Min Mag 8, 37)

(b) Optical properties

(1) Index of refraction In the year 1878 Dufet (C R 86, 881), from an investigation of MgSO, 7aq, N1SO, 7aq, and ZnSO, 7aq, found that the connection between the chemical composition of isomorphous mixtures and their indices of refraction is one of simple proportion ality, so that expressing the results graphically by taking, along two axes at right angles, ordinates proportional to the observed values of μ, and abscissæ proportional to the percentage of one component in the mixture, the resulting curve is a straight line Fock (Z K 4, 583) has, however, taken exception to Dufet's work, and although he finds that the changes in the values of the ordinary and extraordinary ray are proportional to the changes in composition for mixed crystals of SrS2O6 4aq and PbS2O6 4aq, yet in mixtures of thallium and potassium alums, and again in mixtures of MgSO₄ 7aq and MgCrO, 7aq, he could find no such law, v also Fitz and Sansoni (Z K 6, 67) Fock's results have in their turn been questioned by Soret (Z K 11, 197) and Dufet (C R 99, 990) former finds that mixtures of thallium and potassium alum and also of ammonium and potassium alum satisfy the law, while the latter has shown that mixtures of MgCrO, 7aq and MgSO, 7aq are not sufficiently homogeneous for investigations of this kind

Dufet's law probably holds good, but further investigation is needed before it can be considered

esta blished

(11) Optic axis angle Wyrouboff (Bull Soc Min France, 2, 91, 170) has endeavoured to trace the connection between the angle of the optic axis and the chemical composition in the cases of mixtures of K₂SO₄ and Am₂SO₄, and of K₂CrO₄ and K₂SO₄. His results have been expressed graphically by Mallard (Bull Soc Min France, 3, 3), who finds that they give a continuous regular curve, not, however, a straight line if the optical properties of the components are non accordant, those of the mixed crystals will be different from either, v especially Senar mont (lc) on mixed crystals of KNaH₄Cl₄O₄ 4H₂O and (NH₄)NaH₄Cl₄O₄ 4H₂O

	Optic axis plane	1st mean line	2nd mean line
Potassium salt	010	a	c
Ammonium	100	c	h

Starting from the potassium salt and substituting with NH, we observe the following changes, first the obtuse angle diminishes and more quickly for red than for violet light, then at a certain point the axes for red light coincide, while the axes for violet light still lie in 010, the red axes then begin to diverge in 100, the violet

afterwards coincide and follow the red Wyrouboff ($\angle K$ 18, 648), on ammonium and thallium tartrates, gives the following example —

The mixture had always the cleavage and optic axis plane of the ammonium salt, and a crystal containing 88 7 p c of the thallium salt had $2H = 45^{\circ}30'$

(iii) Circular polarisation Bodlander (Z K 9, 309) investigated mixtures of lead and strontium thiosulphates, he found that the rotation varied directly with the composition

(iv) Angle of extinction Max Schuster has shown that the angle of extinction of certain oblique and triclinic mixed crystals, especially the felspars, varies directly with their chemical composition His results have been confirmed by Mallard (Z K 6, 612), who has trewed the subject mathematically

(v) Specific volume relations The specific volumes of mixed crystals appear to depend directly on the relative proportions of their compounds Thus Schroder states (P 95, 441) that

$$V(a\text{CaCO}_3 + b\text{FeCO}_3) = \frac{aV'(\text{CaCO}_7) + bV''(\text{FeCO}_3)}{a + b}$$

where V is the specific volume of the mixed crystal an 1 V', V'' are those of its components. These results have been confirmed by Tschermak (lc) thus

The specific volumes of artificial mixed crystals have been especially investigated by Retgers $(Z \ P \ C \ 3, 497)$ He has studied with great care the mixed crystals formed by $(a) \ K_2 SO_4$ and $Am_2 SO_4$ (b) potassium and thallium alums, he finds that the SG varies directly with the composition, and expressing his results graphically he obtains as his curve a straight line, a result similar to that obtained by Dufet for the values of μ

Formation of mixed crystals by iso dimorphous substances—Two substances, X and Y, are said to be isodimorphous if they each exist in two forms A and B, A' and B', of which A is isomorphous with A' and B with B'

On crystallising a solution containing two isodimorphous substances two series of mixed crystals are obtained, one set having the form A, the other the form B It often happens that the form A of one salt, X say, is stable under ordinary circumstances, while of the other salt, Y, the form B is stable, in the mixed ciys tals of the form A the substance X predominates, in mixed crystals of the form $B, \ Y$ is present in excess In such cases as these a continuous series of mixed crystals cannot always be obtained Crystallisation under these conditions has been especially studied by Rammelsberg (P 91, 321) Thus he finds that MgSO₄ 7aq is rhombic and FeSO, 7aq is oblique, from a solution containing both substances two sorts of mixed crystals are obtained, these do not, however, contain their constituents in all possible proportions, but a gap occurs, the oblique crystals always having more than 1 atom Fe to 2-3 Mg, while the rhombic crystals always contain more than 4 Mg to 1 Fe Another good example is afforded by BeSO, 4aq tetragonal and BeSeO, 4aq rhombic The mixed crystals are tetragonal when S Se > 7 33 1, and rhombic when S Se < 4 1 (Topsoé, Sitz W [2] 66, v also Schulze, A 125, 49, Wyrouboff, Bull Soc Min France, 2, 91)

Cases of crystallisation perfectly analogous to but differing from these have been studied by Rammelsberg (l c), thus copper sulphate usually crystallises in the triclinic system with 5aq, ferrous sulphate in the oblique system with 7aq When solutions of copper sulphate and ferrous sulphate are mixed and allowed to crystallise, two sorts of crystals are got, both of which contain Cu and Fe, as long as the proportion Cu Fe is > 20 1 the crystals possess 5aq and are triclinia, but when there is less Cu the crystals are oblique and contain 7aq

It is very commonly supposed, when two substances closely allied chemically crystallise in different forms but yield two kinds of mixed crystals, that these substances are isodimor phous, although more than one form of each may not be known, v Fock (Z K 6, 160), and note the adverse criticism of Wyrouboff (Bull Soc Min 5, 32)

The specific volumes of isodimorphous substances have been compared by Ri al (B 19, 589), while Retgers $(l\ c)$ has found that in those cases where isodimorphous substances form mixed crystals, each series obeys the law enunciated above, viz that the relative density varies directly with the composition

Constitution of mixed crystals— Since the beginning of the century two opposing views have been held as regards the constitution of these substances

(a) According to the first or physical theory, as we may call it, the most homogeneous mixed crystal really consists of a very intimate mixture of particles of each of the components. This view, held by Hauy, and maintained by Frankenhein n opposition to Berthollet, has recently received the support of Lehmann and Retgors, the latter says that a mixed crystal is a very intimate but purely mechanica mixture of its components, and finds strong confirmation of his view in the fact that the densities, indices of refraction, &c, of mixed crystals vary directly with their composition

(b) The supporters of the second or chemical theory man tain that molecules of each substance come together in the solution to form a complex 'liquid molecule,' while 'liquid molecules' of the same kind unite on crystallisation and form the mixed crystals. Berthollet held this view, which is perhaps more generally accepted than the other, at the present time its chief exponent is Fock, who believes that the formation of mixed crystals and double salts are phenomena of the same order.

Use of mixed crystals as a test of iso morphism—As we have seen, much weight has been attached to this property by Mit scherlich, Kopp, and others, but at the present time so many instances are known of the formation of mixed crystals by substances which can not be considered isomorphous that the test

has lost much of its value (v Lehmann, l c) Retgers (l c) has proposed that only those sub stances should be considered isomorphous, the physical properties of whose mixed crystals vary directly with the chemical composition

Isogonism -Speaking generally we find that if two substances are to be considered isomorphous they must satisfy the two following con ditions (1) they must agree very closely in form and possess similar physical properties, (ii) under suitable conditions they must be capable of forming layer and mixed crystals In Mitscherlich's definition we find, however, a third condition, viz analogy of chemical constitution, and the ques tion arises, How far may two substances which satisfy the two conditions above differ in chemical constitution and still be considered isomorphous? This question has received various answers, thus Scheibler (J pr 83, 273) has announced the isomorphism of most meta tungstates, although they do not all contain the same number of molecules of water of crystallisation, Marignac (C R 55, 888) considers the two following series of substances to be isomorphous -

> K,TiF, H,O CuTiF, 4H,O K,NbOF, H,O CuNbOF, 4H,O K,WO,F, H,O CuWO,F, 4H,O

And he also makes rhombohedral silicotungstic acid, and the acid silicotungstates of Ba and Ca isomorphous Some other similar examples are given by Baker (C. J. 1879, 760). Klein (C. R. 95, 781) believes that the following substances are isomorphous.—

9WO, B₂O, 2H₂O 22aq 9WO, B₂O, Na O 23aq 12WO, B₂O, 4H₂O 29aq (Marignae)

Klein following Marignac, amends Mitscherlich's definition thus Isomorphous substances have either an analogous chemical constitution or a very slightly different percentage composition, in the latter case they contain a group of common elements or elements of identical chemical function, this group making up by far the largest portion of the compound 'It seems however, hardly advisable to widen Mitscherlich's definition, indeed, it is perhaps better if possible to narrow it by defining more closely what is meant by the phrases analogous chemical composition and analogous crystalline form

Substances, such as the double fluorides described by Marignac, are not so much isomorphous as closely related morphotiopically, while from them we may pass through substances exhibiting less and less of chemical analogy to those which agree in form alone, and which may therefore be considered as examples of isogonism (v. Retgers, lc.) As an instance of this we may quote the remarkable analogy noticed by Hjort dahl (C. R. 88, 584) between the crystals of tindimethyl and diethyl chlorides and lead chloride, which all crystallise in the rhombic system, and possess the following axial iatios—

Tin dimethyl chloride 0 8346 1 0 9407
Tin diethyl chloride 0 8386 1 0 9432
Lead chloride 0 8408 1 0 9990

At present it seems that substances which exhibit relations in form and composition may most

conveniently be divided into the following more or less arbitrary groups, between whose limits no

absolute line can be drawn —

(1) Substances very closely related morphotropically, or isomorphous substances—Bodies belonging to this class possess great chemical analogy, crystallise in the same system with nearly the same forms and angles, exhibit a general agreement in the physical properties of their crystals, and often possess the same specific volume, they are, moreover, under suitable conditions capable of forming mixed and layer-crystals Such substances are the sulphates of the group M"SO, 7H,O (M"=Fe", Zn, Mg, Co, Ni) and the alums

(2) Substances closely related morphotropically—To this class belong Marignas's double fluorides, and the substances derived from hydrocarbons by substitution, from them we pass on the one hand to isomerides such as the three dinitro benzenes, which with a minimum difference of chemical constitution possess but little form analogy, and on the other hand to bodies differing but little in form, but showing less and less chemical analogy, till we

reach members of the next class

(3) Isogonous substances, differing greatly in chemical composition but nearly similar in form — To this class belong CaCO, and NaNO, and the substances described by Hjortdahl above, while all substances crystal lising in the cubic system are strictly isogonous (v Sohneke, Entwickelling einer Theorie der Krystallstruktur, Leipzig, 1879)

A H

ISOPRENE o Pentinenes
ISOPYRINE An alkaloid obtained by boiling
the mashed roots of Isopyrum thaluctroides with
water, filtering, evaporating to a syrup, ppg with
ammonia, and extracting with ether (Hartsen,
C C 1872, 523) White powder with bitter taste,
forming an amorphous hydrochloride

Pseudo-isopyrine After the roots have been boiled with water they still contain this alkaloid, which may be extracted with alcohol After removing the alcohol by evaporation ammonia is added to the aqueous residue, and the ensuing pp treated with ether, whence pseudo isopyrine separates in needles. It is ppd from its solution as hydrochloride by adding very dilute HClAq and ammonium chloride (difference from isopyrine)

ISURETIN v FORMAMIDOXIM

ITABROMOPYROTARTARIC ACID v Bromo

ITACHLOROPYROTARTARIC ACID & CHLORO-PYROTARTARIC ACIDS

ITACONIC AGID $C_3H_4O_4$ to $C_4H_4(CO_2H)_2$ or $CH_2(CO_2H)$ $CH_2(CO_2H)$ $CH_2(CO_2H)$ (?) Mol w 130 [161°] S G 1 6 (Schröder, B 13, 1072) S 5 at 10°, 8 at 20° S (88 pc alcohol) 25 at 15° (Baup) R_{∞} 44 25 (in a 4 18 pc aqueous solution) (Kanonnikoff, J pr [2] 81, 348) H C 476,580 (Louguinine, O R 106, 1291) Heat of solution 5,923 (Gal a Werner, Bl [2] 47,160) Heat of neutralisation 25,725 (G a W) Shown by Raoult's method to be isomeric and not polymeric with citraconic and messaconic ands (Paterno, B 21, 2156)

Formation—1 By the action of heat on entrie acid, aconitic acid being first formed (Baup, A. 19, 29, Crasso, A 34, 63)—2. By

heating itamalic acid $C_bH_aO_a$ (Swarts, Z 1867, 649)—3 By heating citric acid with water at 160° (Markownikoff a Purgold, Z 1867, 264)—4 By heating aconitic acid with water at 180° (Pebal, A 98, 94)—5 By heating citraconic anhydride with water under pressure (Fittig, A 188, 72)

Preparation —1 Coarsely-powdered catric acid (125 g) is anistilled from shallow retorts completely filled with it as quickly as the frothing will allow, the cily distillate is separated from the water as completely 21 possible and left to crystallise (Meilly, A 171, 153, cf Wilm, A 141,28) A temperature of 160°-175° is favour able to the formation of itaconic acid, at a very high temperature it is mostly converted into catraconic anhydride—2 Citraconic anhydride (2 vols) is heaten with water (5 vols) at 150° for 7 hours, and the produce poured into flat dishes and left to crystallise (Fittig, A 188, 72)

Properties — Trimetric octahedra (from water) Strongly and Sol ether When heated above its melting point it is resolved into citra conic anhydride and water Ammonium itaconate gives a brown pp with FeCl. soluble in excess of FeCl_s, but reppd on boiling, and redis

solved on cooling

Reactions —1 Combines with bromine, form ing ita-di-bromo pyrotartaric acid (Kekulé, A Suppl 1, 338, 2, 111, Cahours, A Ch [3] 67, 129) - 2 Chlorine forms ita di chloro pyrotar taric acid -3 Heated with aqueous HBr, HCl, and HI, combination takes place with produc tion of ita bromo-, ita chloro-, and ita iodo pyrotartaric acids Excess of HI produces pyrotar taric acid (Bl [2] 4, 374) —4 Sodium-amalgam reduces it to pyrotartanic acid (Kekulé) -5 HOCl gives chloro-itamalic acid C,H,ClO, -6 Anhy drous HCy at 145° apparently forms an addi tion-product, which, when distilled, gives citra conic acid (Barbaglia, B 7, 465) -7 Heated with aqueous K.SO, it forms a gummy salt, pos sibly sulphopyrotartaric acid C, H, SO, (Wieland, A 157,34)-8 The electrolysis of the potassium salt yields a mixture of gases, apparently containing propylene and acetylene, out not allylene CH₂ C CH₂ (Béhal, A Ch [6] 16, 366, cf Aar land, J pr [2] 6, 256) -9 Cold HNO, gives off no CO₂ (Franchimont, R T C 3, 422)

Constitution — The molecular weight is shown by Raoult's method to be the same as that of citraconic and of mesaconic acids According to Aarland potassium itaconate gives a different allylene on electrolysis from that derived from the potassium salts of citraconic and mesaconic acids, this would lead to the formula CH₂ C(CO₂H) CH₂ CO₂H Béhal, however, was unable to confirm Aarland's experiments According to Knops (A 248, 228) the molecular refraction of the itaconic ethers indicates one C C group Itaconic acid resembles mesaconic acid, but differs from citraconic acid in requiring heat to enable it to combine with HBr and with bromine Itaconic acid reacts with aniline, but not with dimethylaniline

Salts —KHA"aq lustrous laminæ, v sot water — *K,A" does not crystallise — (NH,)HA". tables S 80 at 12° — (NH,)HA"aq needles — BaH,A",2aq —BaA"aq (Petri, B 14, 1634) — CaH,A",2aq S 77 at 12° —CaA"aq needles. S 22 at 18° — SrA"aq —PbA"aq —PbA"PbO

IVY. 97

(Otto, A 127, 181) -Ag, A" almost insol bc ling water

Methyl ether MeA" (212°) SG 11 1899 (Anschutz, B 14, 2784), 1 1241 (Knops) R_{cc} 60 44 Oil Polymerises, changing to a solid

in which $R_{\infty} = 57.7$

Et₂A" Ethylether (229°) 1051 (Anschütz), 25 10415 (Knops, A 248, 210) $R_{\infty} = 75.52$ Polymerisea $R_{\infty} = 70.59$ From silver itaconate and EtI (Swarts, Bull Acad royal Belgique [2] 36, No 7) Formed also by passing HCl into a solution of itaconic acid in alcohol Colourless oil Changes in a few days into ... viscid liquid, and ultimately into a brittle, glassy mass, which is completely decomposed on distillation

Chloride C.H.(COCl), (87°) at 17 mm From the annydride and PCl, Colourless pun Converted by water into itaconic gent ligad

acid (Petri)

 $Anhydride C_{2}H_{1}(C_{2}O_{3})$ [68°] (148°) at 30 mm Occurs among the products of the dis-tillation of citric acid Prepared by the action of AcCl on itaconic acid (Anschutz, B 13, 1539) or on silver itaconate suspended in ether (Markownikoff, B 13, 1844) Trimetric prisms a b c = 617 1 455 Sol chloroform Slowly dis Trimetric prisms, solves in water with formation of itaconic acid When distilled under atmospheric pressure it changes into the isomeric citraconic anhydride

Amide C,H,(CONH₂)₂, [192°] From Me₂A" and aqueous NH₂ (O Strecker, B 15, 1639) Small colourless crystals (from water)

hot water, m sol alcohol, insol ether Mono anilide C,H4(CO,H)(CONHPh) or

CO'H CH CH' CO (3) Itaconantlic acid [189°] Formed by heating itaconic acid (5 g) with water (50 g) and aniline (3 g) to boiling for half an hour, and depositing on cooling as crystals (Michael a Palmer, Am 9, 200, Gottlieb, A 77, 265) Formed also by allowing a solution of acid aniline itaconate to stand for several days in the cold Needles (from water) Insol dilute HClAq, sol dilute alkalis, and reppd unchanged by acids —BaA'₂ (at 170°) —CuA'₂ (at 160°) — AgA

Mono-anilide C₃H₄(CO₂H)(CONHPh) (?) [151 5°] From itaconic anhydride and aniline (Anschütz, B 20, 3215, 21, 958) Not identical

with the preceding

Anilide C,H4(CONHPh), [185°] Formed by heating aniline itaconate, or a mixture of ita come acid, with excess of aniline at 180° (Gottlieb, A 77, 282, O Strecker, B 15, 1639) thin plates, sol alcohol and ether, sl sol water A mixture of HNO, and H,SO, converts it into an amorphous penta nitro-derivative (Gottlieb, A. 85, 40)

Chloro-itaconic acid CaHaClO Formed by heating aconic acid C,H,O, with HCl (Swarts, J 1873, 584) Crystailine crusts, sl sol cold water Reconverted by boiling water into aconic acid

Bromo-itaconic acid C,H,BrO, [164°] Formed by the dry distillation of its di bromopyrotartario acid C.H.Br.O. (Swarts, Bull Acad roy Belgique [2] 83, No 1) Also by heating aconic acid with HBr Its anhydride is similarly formed from ita-di bromo-pyrotartaric anhydride (Petri) Crystals resembling itaconic acid (from Vol. III

water or by alkaline carbonates into HBr and aconic acid Reduced by tin or zinc to itaconic acid

ITAMALIC ACID v OXY-PYROTARIARIC ACID.

ITAPYRUVIC ACID C4H6O2 Obtained, to gether with water and CO₂, by distilling statartaric acid at 125°-170° (Wilm, A 141, 37) Viscid mass, v sol water and alcohol, volatile with steam —BaA', aq (at 100°) glassy amorphous mass —PbA', hygroscopic amorphous mass, sl sol water The silver salt is soluble, but very decomposable

ITATARTARIC ACID C.H.O. Dr-oxy-pyrotartaric acid Formed by gradually adding a solution of HOCl to one of sodium itaconate (2 p c solution) at 0° in the dark, and boiling the resulting solution of chloro oxy pyrotartaric acid The acid is ppd as lead salt, which is subse quently decomposed by H2S (Wilm, A 141, 28 Morawsky, J pr [2] 10, 00, 11, 200, also by warming ita di bromo pyrotartaric acid with Ag_2O (Kekulé, A Suppl 1, 346) Amorawarana witroons deliquescent mass V e sol water and alcohol, not volatile with steam Split up by dry distillation into CO₂ and itapyruvic acid. The alkaline salts prevent the ppn of ferric and cupric salts by alkalis - CaA" 1/2 aq crystalline mass, sl sol water -BaA" (at 100°) amorphous, v sol water, and ppd from aqueous solution by alcohol —PbA" aq tablets, v sl sol water —Ag₂A" bulky pp, sol water, but decomposed on boiling its solution

IVAIN C24H42O2 Occurs in Iva, the leaves and stem of Achillea moschata gathered before flowering (Von Planta, A 155, 150) The volatile oil is first removed by distillation, and the residue is dried and extracted with alcohol, the filtrate is ppd with lead acetate, freed from lead by H2S, and evaporated Dark yellow resinous mass, msol water, v sol alcohol The alcoholic solution has an extremely bitter taste

When my leaves, col-IVY Hedera Helix lected in December, are bruised, exhausted with water, and then treated with alcohol, the alcoholic extract contains a glucoside C₃₂H₃₄O₁₁ This may be obtained by evaporating the alcohol, extracting the residue with benzene, and then with acetone, which deposits the glucoside on cooling (Vernet, C R 92, 360) It forms mammillary groups of silky colourless needles with slightly sweet taste and neutral reaction. It melts at 233°, and at 22° its alcoholic solution has a leworotatory power of $[a]_p = -47.5^{\circ}$ It is insol water, chloroform, and petroleum, al sol acetone, benzene, and ether in the cold, but readily soluble in these liquids when hot. V sol boiling alcohol Sol cold alkalis The glucos ide has no action on Fehling's solution, but on boiling with dilute H2SO, a sugar is formed which crystallises by slow evaporation of its alcoholic solution in bulky transparent crystals with decided sweet taste, and reduces Fehling's solution, but is not fermented by yeast. The rota bry power of a cold solution of this sugar is $[a]_{D} = +98.6^{\circ}$ immediately after it preparation, but some hours afterwards it has been found to fall to [a]_D = 76 2 Besides the sugar, there is formed in the hydrolysis of the glucoside a water), v sl. sol cold water, resolved by boiling neutral body C. H.O. [2780-2800], which crystallises in slender prismatic needles, without | ening to a hyscintu-red solid, which forms a taste, m sol. alcohol, insol. alkalis, and dextro-

rotatory [a]_D = 42 6°
IXOLITE A fossil resin found in a bed of bituminous coal at Oberhart Fluid drops, hard887)

yellowish powder SG 1008 Softens at 76° Yields pyrocatechin on fusion with potash (Haidinger, P 56, 345, Weidel, Sits W [2] 74,

J

JABONINE C.H.14N2 16 CH≪N-CH>C CHMe NMe₂. Dr - methyl -

amido ethyl pyridine (235°-240°) Formed by distilling pilocarpine or pilocarpidine with baryta (Hardy a Calmels, Bl [2] 48, 231) The crude product is evaporated several times with HClAq and the base set free with KOH Colourless oil with feetid odour Its hydro-chloride forms confusedly crystalline masses The double salts B'HAuCl, B'AuCl, B'2PtCl, and B'2H2PtCl, are all amorphous

JABÓRANDI The native name for several drugs of a sudorific and salivating character, consisting of the leaves and twigs of various species of Pilocarpus and other trees growing in Brazil, Pernambuco, and Paraguay (Holmes, Ph. [3] 5, 581, 641, Schelenz, Ar Ph [3] 7, 414, Baillon, Ar Ph [3] 7, 327) Jaborandi leaves contain pilocarpine (Byasson, Ph [3] 5, 826, Hardy, Bl [2] 24, 497), which readily changes to jaborine (H Meyer a Harnack, A 204, 67) The latter acts like atropine, and is an antidote to pilocarpine Pilocarpine C₁₁H₁₆N₂O₂ gives with MeI a methylo iodide Pilocarpidine C₁₀H₁₄N₂O₂ is also present in jaborandi (Harnack, A 238, It is crystalline but extremely deliques-It is alkaline, and turns yellow in light cent V sol alcohol, m sol water, sl sol ether sulphate and hydrochloride are deliquescent, its nitrate forms crystals resembling KNO, platinum salt B', H, PtCl, is crystalline It readily changes when exposed to light into a base jabor tidine $C_{10}H_{12}N_{..}O_{.0}$, which has an amorphous platinum salt The jaborandine of Chastaing (C Rnum salt 94, 968) obtained from pilocarpine and HNO, is probably jaboridine (Harnack, A 238, 238) The jaborandine of Parodi (Revista farmaceutica, 1875, 3) from Piper reticulatum CieH12N2O3 may be the same

JABORIC ACID C₁₀H₂₂N₂O₃ te C₅H₄N CMe(OH) CO O NMe, CMe(C₅H₄N) CO₂H Formed, together with NMe, jaborine and pilocarpidine, by rapidly heating pilocarpine to 175°, and keeping it at that temperature for half an hour If the product be extracted with baryta water and the extract shaken with ether, the ether will contain jaborine, while pilocarpidine and jaboric acid remain in the aqueous solution In this solution, after removing barium by CO₂, AgNO3 forms a curdy pp of C10H24N3O3Ag2NO3, whence H2S removes the silver (Hardy a Cal mels, C R 102, 1251, Bl [2] 48, 225) ous mass, v sol. water Not removed fron its aqueous solition by ether With alkalis it forms gummy salts, sol water and alcohol, and not de composed by CO₂. Hot conc KOHAq or boil ng HClAq converts it into pilocarpidine and oxypyridyl propionic acid C₂H₄N CH₂ CH(OH) CO₂H

Salts - AgA' brown powder, ppd by adding alcohol to a solution of the acid to which a limited quantity of AgNO₃ has been added — AgA'AgNO₃ curdy pp — A₂PtC₁, viscous pp — A'₄(PtCl₄)₃ yellow powder — A'₄H₂PtCl₆ sticky A'₄(PtCl₄), yel pp —A'(AuCl₃).

JABORIDINE C10H12N2O3 Formed by fre quently evaporating pilocarpidine with acid (Harnack, A 238, 234) Syrup, sol water, m sol ether Acts physiologically like jaborine though weaker Its hydrochloride is syrupy, and v sol water -B', H2PtCl, (dried at 100°) [110°-120°] Amorphous

JABORINE C.H.,N.O. te NMe. CMe(C,H,N) CO O NMe. CO CO CMe(C,H,N) NMe. (?) Occurs in jaborandi, and in false jaborandi (the leaves of Piper sticulatum) Prepared as described under Jaboric acid Brittle resin Insol water, v sol ether, sol alcohol Dissolves in a solu tion of jaboric acid Dissolves in HClAq, and is reppd by KOH as a curdy pp which readily Boiling conc agglomerates under warm water KOHAq converts it into pilocarpidine Boiling HClAq does the same Poisonous, acting like atropine

Salts -The hydrochloride is amorph ous, and v e sol water and alcohol -B PtCl. dirty white gelatinous pp —B'PtCl, yellowish white pp —B'H₂PtCl_g -B'(AuCl_s)₂ (Hardy a Cal

mels, C R 102, 1251)

JALAP The roots and tubers of certain convolvulaceous plants which rield purgative Officinal jalap consists of the tubers of Convolvulus Schiedanus, which contains Con volvulin, a strongly purgative resinous glucoside Jalap wood or jalap stalk (Stipites Jalapæ), the root of C orizabensis, contains a different glu coside, Jalapin (Kayser, A 51, 100, cf Mayer, A 95, 161)

JALAPIN $C_{24}H_{36}O_{16}$ or $C_{68}H_{112}O_{32}$ [150°] Oc curs in the root stalk of Convolvulu. (or Ipomæa) orizabensis, and forms the principal portion (soluble in ether) of the jalap regin prepared therefrom (Johnston, P T 1840, 342, P M [3] 17, 183, Kayser, A 51, 101, Mayer, A 83, 122, 95, 129, Haule, Rep 48, 365, Planche, J Ph 13, 165, 24, 169, Weppen, N Br Arch 87, 153, Chevallier, J Ph 9,306Occurs also in the resin in scammony root from Convolvulus Scammonia (Johnston, P T 1840, 340, Keller, A 104, 63, 109, 209, Spirgatis, A 116, 289, Planche, J Ph 13, 165, 18, 183, Marquart, N Br Arch 7, 248, 10, 139)

Preparation—1 Jalap resin is dissolved in

a large quantity of alcohol, water is added until the liquid becomes slightly turbid, and the whole boiled with animal charcoal, filtered, ppd by lead acetate and a little ammonia, filtered, freed JECORIN 99

from lead by H₂S, the alcohol distilled off, and the residue kneaded in boiling water, and the jalapin finally extracted with ether (Mayer)— 2 Finely powdered jalap resin is mixed with sand and extracted with ether, which deposits the jalapin on evaporation (Stevenson, Ph [8] 10, 644)

Properties — Colourless amorphous resin Softens at 123°, and relts at 150° Tasteless V al sol. water, v e sol alcohol, ether, and chloroform, sol benzene, oil of turpentine, petroleum, and HOAc Cone H₂SO₄ dissolves it slowly in the cold, acquiring in a few minutes a maroon colour, bu. finally becoming black With K₂CrO₄, KMnO₄, KClO₅, or KNO₅ there is a brown colour and a smell of rancid butter, while MnO₄ gives a dark green col. ur (Stevenson)

MnO, gives a dark green col. ur (Stevenson)

Reactions - 1 Boiling dilute HCl splits it up
into sugar and jalapinol - 2 Boiling aqueous
alkalis convert it into jalapic acid - 3 Nitric

acid forms ipomic and oxalic acids

Jalapic acid C₃₄H₅₀O₁₈ or C₆₈H₁₁₈O₂₈ [120°] Formed by dissolving jalapin in aqueous alkalis (W Mayer, A 92, 125, 95, 129, Spirgatis, A 116, 289) Prepared by boiling jalapin with baryta-water until the solution is no longer ppd by acids, the baryta is then removed by H₂SO₄, the excess of sulphate by lead hydrate, and the excess of lead by H₂S Jalapic acid is then de posited on evaporating Translucer, amorphous, yellowish, brittle mass Softens below 100°, and melts about 120° Has no smell, but an irritating taste and strong acid reaction. V e sol water, v sol alcohol, m sol ether In neutral solutions it is ppd by lead subacetate, but not by any other metallic salt

Reactions —1 1 uming HCl splits it up into palapinol and glucose According to Spirgatis the products of hydrolysis of jalapic acid (and jalapin) derived from scammony are jalapinolic acid and glucose —2 Boiling dilute HCl forms (a) jalapic acid, so called (Mayer) —3 HNO, gives ipomic, oxalic, and isobutyric acids —4 KMnO, gives isobutyric, oxyisobutyric, and oxalic acids (Poleck a Samelson, C C 1884,

813)

Salts — Jalapio acid displaces CO₂ from aqueous Na₂CO₂.—Ba(C₂₄H₁₀O₁₅)₂ obtained on evaporating a solution of jalapic acid mixed with a slight excess of baryta-water after removing excess of baryta by CO₂ Amorphous — Ba₂(C₂₄H₃,O₁₆)₂ obtained by using baryta (2 pts), and jalapic acid, passing CO₂ through the boiling solution, filtering and evapo-

rating Amorphous mass [100°]

(a) - Jalapic acid, so called C28 H 50 O 15 Formed, in small quantity, in the hydrolysis of lalapic acid by HClAq or dilute H2SO, (Mayer) On cooling it separates with the jalapinol as a soft brown amorphous mass, which is then boiled with baryta water, and the resulting solution de posits barium je apinolate on cooling When the mother liquor is concentrated silky needles of the Ba salt of '(a) jalapic' acid are obtained salt is decomposed by a retic acid. White flexible needles, melting below water at 80° Feebly acid. in reaction Sl sol cold, m sol hot, water, v e sol alcohol and esuer solit it up into jalapinol and glucose HNO, and oxalic acid. Potashe sol alcohol and ether Boiling dilute acids gives apomic acid and oxalic acid. Potash-fusion forms palapinolic acid and oxalic acid.

from lead by H₂S, the alcohol distilled off, and | Ba(C₂₂H₄₀O₁₈)₂: White needles, sol. water and the residue kneeded in holling water, and the | alcohol

JALAPINOL C₂₂H₄₂O₇. [62°] Formed, together with sugar, by the hydrolysis of jalapin and of jalapine acid (W Mayer, A 95, 145) C₄₂H₁₁₂O₄₂+11H₄O = C₄₂H₄₂O₇+6C₄H₁₂O₄. Prepared by allowing a solution of jalapine acid (2 vols) mixed with fuming HClAq (1 vol.) to stand for a few days, washing the crystalline product with water, and recrystallising from alcohol, with use of animal charcoal, whence it separates in cauliflower like groups of crystals. Insol cold, v sl sol boiling water, v sol alcohol and ether Aqueous alkalis convert it into jalapinolic acid KMnO₄ forms isobutyric acid and (by further oxidation) oxyisobutyric acid (Poleck a Samelson, J 1884, 1447)

JALAPINOLIC ACID C₁₄H₁₄O₅ [64°] Formed by treating jalapinol with aqueous KOH, ammonia, or baryta Formed also by fusing jalapin or jalapin acid with KOH (Mayer, A 95, 145, Spirgatis, A 116, 306) According to Spirgatis it is also produced, together with sugar, by the action of mineral acids on jalapin and jalapic acid derived from scammony Poleck and Samelson (J 1884, 1447) by the action of alcoholic potash on jalapinol obtained, together with iso butyl alcohol, a jalapinolic acid C₁H₂₀O₄ White tufts of minute thin four sided prisms Insol water, v sol alcohol and ether Lighter than water Has an acid reaction Nitric acid oxi

dises it to ipomic acid and oxalic acid

Salts—(NH₄)HA'₂ cauliflower heads of minute needles—NaA' (dried at 100°) slender needles—BaA'₂ (dried at 120°) minute thin white needles, nearly insol cold, sl sol boiling, water, m sol boiling alcohol—CuA'₂ (dried at 100°) greenish blue pp formed on mixing hot aqueous solutions of sodium jalapinolate and CuSO₄ (Spirgatis)—Cu₄A'₂(OH)₂ (dried at 100°) Ppd by adding aqueous cupric acetate to a slightly alkaline solution of ammonium jalapinolate Amorphous dark bluish-green mass—PbA'₂ Ppd by adding lead acetate to an alcoholic solution of jalapinolic acid mixed with a little ammonia White amorphous mass—AgA' From aqueous AgNO₄ and alcoholic ammonium jalapinolate Flocculi

Ethyl ether EtA' [325°] From the acid (or from scammony) by saturation of the alcoholic solution with HCl, and ppg with water

Flat tables

JAMEOSIN C₁₀H₁₃NO₃ [77°] Occurs in the bark of jambosa root (the root of Myrtus jambosa?), from which it may be extracted with ether (Gerrard, Ph [3] 14, 717) White tasteless crystals, sol cold ether, alcohol, chloroform, and hot petroleum ether Insol cold, sol boiling, water Conc H₂SO₄ gives a bright green colour changing to reddish brown Is not a glucoside. Does not form salts with bases Has no medianal properties

JAPACONINE v Aconite alkaloids JAPACONITINE v Aconite alkaloids JAVANINE v Cinchona bases

JECORIN C₁₀₅H₁₈₃N₃SP₂Na₃O₄₆ (?) A substance obtained from liver (Drechsel, *J pr* [2] 33, 425) Occurs also in ox spleen, human brain, and horse's muscle (Baldi, *Ar Physiol* 1887, *Suppl* 100) Amorphous substance Hygroscopie, insoluble in dry ether, soluble in wet ether, v sl

100 JECORIN.

sol alcohol Swells up in water forming a sticky mass, which separates into a clear solution and app The latter dissolves in much water Not ppd by boiling, ppd by NaCl Prevents ppn of cupric salts by NaOH, forming a blue solution, and on boiling app of Cu₂O Boiling HCl dearning amongst other products The latter dissolves in much water Not composes it, forming amongst other products stearic acid

JERVIC ACID An acid occurring in white hellebore root (Veratrum album) (Weppen, Ar Ph. [3] 2, 101, 198), found by E Schmidt (Ar Ph [3] 24, 513) to be identical with chelidonic aoid

JERVINE C₂₀H₃,NO₃ (Wright a Luff), C₂₁H₄,N₂O₃ (Tobien) or C₃₀H₄₀N₂O₃ (Will) [237°] (W a L) An alkaloid occurring in the rhi-magnes of Veratrum album (Weppen, Ar Ph [3] 2, 101, 193, Simon, P 41, 569, Mitchell, Ph [3] 4, 796, Bullock, Ph [3] 6, 1009, Wright a Luff, C J 85, 407), and of V lobelranum (Tobien, Ph [3] 8, 808) and V viride (Bullock, Ph [3] 10,

Preparation - The extract obtained with al cohol containing tartaric acid is used several times to macerate fresh portions of the root, freed from alcohol by distillation, mixed with water, frac tionally ppd by NaOH and taken up by ether The base first ppd is pseudojervine, and is the least soluble in ether Other fractions contain jervine, rubijervine, and veratralbine (Wright a Luff)

Properties -Loosely coherent crystals (containing 1 aq or 2aq) (from alcohol) Almost insol water, sol alcohol, v sl sol ether (when pure), insol ligroin Cone H₂SO₄ forms a yellow solution changing through brown to greenishbrown Boiling alcoholic KOH has no action

Salts - The hydrochloride is crystalline, sl sol water, v sl sol HClAq (Will, A 35,116) According to Tobien it gives a rose colour when warmed with nitric acid. The nitrate and sulphate are sl sol water -B H2PtCl4 (Will) -B'HAuCl, -The acetate is sol water

Rubijervine C₂₈H₄₃NO₂ [236° cor] Anhydrous crystals (from alcohol) Dissolves in conc H₂SO₄, forming a yellow solution changing to brownish-red The sulphate is crystalline, v sol cold dilute H.SO, sl sol cold water The hydrochloride is crystalline and v sol water - B'HAuCl,

Pseudojervine C₂H₄₅NO, [209°] Crystals V sl. sol ether Reacts with conc H₂SO, in the same way as jervine Not affected by boiling al coholic KOH —B'HCl 2aq crystalline, v sl sol hot water, m sol dilute HClAq —The sulphate 18 sl sol cold, v sol hot, water -B'HAuCl,

Veratralbine C22 H43 NO Amorphous resinous base Conc H2SO, forms a yellow solution turning crimson and exhibiting green fluorescence Alcoholic potash does not saponify it Its salts are amorphous

HC C(OH) C CO CH JUGLONE C. H.O. 1.6

HC CH — C CO CH Oxy (a) naphthogumone Nucin. Regionin [154°] Formed by the oxidation of (a) hydrojugione which occurs in the green shell of the walnut (Vogel & Reischauer, C C 1858, 543, B 10, 1544, Phipson, C R 69, 1872, C N 52 89, Mylius, B 17, 2411) Formed also by allowing (1,4')-di-oxy-naphthalene to stand for 24

hours inixed with k2Cr2O, and dilute H2SO.

(Bernthsen a Semper, B 20, 984)

Preparation — Dry ripe walnut shells are The etherepeatedly extracted with cold ether real solution is shaken with a dilute solution of CrO₃ (10 pts_K₂Cr₂O₇ + 18 pts H₂SO₄ in 500 pts. of water) The ether is distilled off, and the residue, after removing tarry impurities by boiling with a little ether, in crystallised from a mixture of chloroform and ligroin The yield is 150 grms from 100 kilos (Bernt'isen a Semper, B 18, 204)

Properties — Thin glistening red prisms or needles Sublimable in small quantities Somewhat volatile with steam Ēasily soluble in chloroform and acetic acid, sparingly in ether, ligroin, and cold a cohol, almost insol water It stains the skin brown Dissolves in dilute NaOH with a fugitive purple colour, in H_aSO₄ with a blood red colour It is decomposed by hot water or hot acids By boiling with HNO₄ it is oxidised to a di nitro oxy phthalic acid. On heating with water or HCl it decomposes into insoluble amorphous bodies. Its alkaline solution is oxidised by the air to oxy juglone C10H.O4 With aqueous dimethylamine it gives dimethyl amidojuglone C10H3O3(NMe2), and with alcoholic aniline it gives phenyl amido juglone $C_{10}H_3O_3(NHPh)$ On fusion with KOH it yields m oxy benze c acid (Mylius, B 18, 463) Finely powdered juglone gradually added to an alkaline solution of hydrogen peroxide is oxidised to c oxy phthalic acid (B a S) Juglone and its oxim do not dye materials mordanted with metallic oxides (Kostanecki, B 22, 1347) Jug lone yields naphthalene when distilled with zinc dust Reducing agents yield (a) hydrojuglone

Salt -(C10H2O3)2Cu nearly insoluble mi-

croscopic violet prisms

Acetyl derivative C10H3O2(OAc) [155°], flat yellow tables or thin prisms, sublimes in long thin plates, volatile with steam, sparingly soluble in water and cold alcohol, easily in hot alcohol, ether, benzene, chlorofor n, and CS2, yields an intense green colouration with alcoholic KOH

Mono oxim C₁₀H₃(OH) $\left\{ egin{array}{l} O \\ NOH \end{array} \right.$ Glistening red needles or thin prisms, easılv soluble in alcohol and acetic acid, very slightly in water, dissolves with a blood red colour in H,SO, and in dilute NaOH (Bernthsen a Semper, B 18, 203)

Droxim C₁₀H₁(OH)(NOH), From juglone (1 mol) and hydroxylamine hydrochloride (2 mols) at 140° (Bernthsen a Semper, B 19, 168) Brownish yellow needles (from HOAc) Puffs off at 225° Sl sol. alcohol and acetic acid Alkalis dissolve it, forming an orange solution

Phenyl-amido juglone C₁₀H₂O₂(NHPh) [230°] Formed by heating an . lcoholic solution of juglone and amline (Mylius, B 18, 472) Red tables Sublimable V sl sol alcohol Dissolves in alkalis with a purple red colour

Di-methyl-amido-juglone O₁₀H₁O₂(NMe₂) [150°] Formed by dissolving juglone in dimethylamine solution (Mylius, B 18, 464) Brownish violet tables Soluble in bensene, chloroform, and CS, sparingly in alcohol, ether, and acetic soid, insoluble in water By SnCl, it is reduced to dimethylamido hydrojugione; On | soluble in benzene, sparingly in alcohol and heating with strong HCl it splits off dimethyl-

Oxyjuglone CioH.O. 2 6 CH C(OH) C CO C(OH)

. Di-oxy-naphthoquin-CH CH — Č CO ĆH one [c 220°] Formed by heating di methylamido juglone with Hell Formed also by oxidation of an alkaline solution of juglone by exposure to the air Prepared by oxidation of juglone with an alkaline solution of potassium ferricyanide, yield 50 pc of theory (Mylus, B 18, 466) Small yellow trimetric tables Spa ringly soluble in alcohol, ether, benzene, and

 CS_2 Salts $-A''Na_2$ easily soluble red needles -A"K, sparingly soluble red needles -A"Ag. ∆"Ci amorphous red pp

Bensoylderivative C₁₀H₄O_z(OBz) [170°], small yellowish white crystals, easily

acetic acid, insoluble in water

JUGLOXIM v Oxim of JUGLONE.

JUGLONIC ACID v DI NITRO-OXY PHTHALIC ACID

JUNIPER OIL The berries of the juniper, which are used for flavouring gin, yield on distillation an essential oil C₁₆H₁₆ (155°-163°) S G 25 839 (Blanchet, A 7, 165, Souberran a Capitaine, A 34, 325) The oil is lævorotatory, it

gives no solid bromide, but after heating the oil to 260° it is partly changed to a product boiling about 180°, and this gives cinenetetrabromide According to Wallach (A 227, 288) it contains pinene (v Terpenes) The product of distilla tion of the wood of the juniper contains a sesquiterpene C15H24, which forms a hydrochloride C13H24H2Cl2 melting at 118° (Wallach, A 238, 82)

JUTE v CELLULOSE.

ĸ

KACOTHELINE C₂₁H₂₂O₉N₄ (not C₂₀H₂₂O₉N₄) • c C21H22(NO2)2O3N2 Prepared by dissolving brucine in an excess of cold nitric acid (1, 2 8 G) and warming to 50°-60° till the solution has be come yellowish red, the kacotheline separates out in small crystals (cf vol 1 p 654) oxidation with CrO, and H₂SO, it yields the same product O₁₀H₁₈N₂O, as brucine By treatment of kacotheline, suspended in boiling HCl, with bromine water it is converted into an acid This acid by further oxidation with C₁₉H₂₄N₂O₃ CrO, and H,SO, yields the above oxidation pro duct $C_{14}H_{18}N_2O_4$ On reduction with tin and HCl at yields a base $C_{21}H_{22}(NH_2)N_2O_4$ (Hanssen, B 20, 452)

Base $C_{21}H_{23}N_{2}O_{4}$ to $C_{21}H_{23}(NH_{2})N_{2}O_{4}$ [232°] Formed by reduction of kacotheline with tin and HCl Needles Atmospheric oxidation or Fe₂Cl₄ produces a blue black colouration Insoluble in water and alcohol, dissolves in aqueous NaOH with a reddish yellow colour Its methylo iodide forms glistening plates easily soluble in water -B"H2Cl, large glistening crystals (Hanssen, B

KAÍRINE v (B 4) OXY (Py 4) METHYL-QUINOLINE TETRA HYDRIDE

Kairine A ϵ (B 4) Oxy (Py 4) ETHYL QUIN OLINE TETRA HYDRIDE

KAIROCOLL C,,H,,NO, t.c.

CH, CO, H Sol alcohol and ether, sl sol water Prepared by heating (B 4) oxy quinoline tetra hydride with chloro acetic acid (O Fischer, B 16, 718)

KAIROLINE is described as METHYL-QUINOL-INC TETRA-HYDRIDE

Amido-kairoline v Amido (Py 4) methyl-

QUINOLINE TETRAHYDRIDE Mitro-kairoline v NITBO-(Py 4)-METEYL-

QUINOLINE TETRA-HYDRIDE

KAIROLINE m CARBOXYLIC ACID (Py 4) Methyl quinoline tetra hydride (B 3)-CARBOXYLIC ACID

KAKOSTRYCHNINE v CACOSTRYCHNINE.

KAMALA A yellow dye, used in India, con tained in the seed capsules of Mallotus philhpensis, and occurring in commerce as a yellowish brown powder composed of minute resinous globules It contains Mallotoxin (q v) (A. G a.

W H Perkin, jun, B 19, 3109)

KAORI GUM The product of a coniferous tree (Dammara australis) growing in New Zes-When distilled with steam it yields a terpene C10H16, (157°-158°), S G 15 863 (Rennie, C J 39, 240, cf Thomson, A Ch [3] 9, 499; Mur, C J 27, 733) It is feebly laworotatory, and yields a small quantity of cymene when

treated with PCl,

KAWAIN A crystalline resin, occurring along with METHYSTICIN $(q \ v)$ in Kawa kawa, the root of Macropiper methysticum (Gobley, J Ph. [3] 37, 19, O'Rorke, C R 50, 598, Cuzent, C R 50, 436, 52, 206, Nölting a Kopp, Monst. 50, 436, 52, 206, Nölting a Kopp, M Scient [3] 4, 9, 20) It is not a glucoside oxidation it yields benzoic acid

KELLIN A glucoside in Ammi Visnaga (Mustapha, C R 89, 442) Small silky needles, v sl sol cold water, sol alcohol, v sol ether. Has a bitter taste Gives a white pp with Nessler's reagent Emetic and narcotic

KEPHIR v MILE

KERATIN v PROTEIDS, Appendix C KETATES (ethers of ketones) Bodies constructed on the type $\stackrel{X}{Y} > 0 \stackrel{O}{\stackrel{R'}{\circ}}$ (Morley a. Green, B 17, 8015) Bodies of the lorm X > C < SR' or X > C < SR'' may be calledthioketates

A name given by V Meyer and KETINE Treadwell (B 14, 1150, 15, 1059, 1055) to the product of the reduction of nitroso-acetone with tin and HCl Its di-carboxylic ether is formed 102 KETINE.

in like manner by reducing nitroso-aceto-acetic ether Ketine C.H.O. appears to be di-methyl-CH. N CMe CH N CMe

, and will be pyrazine or | CMe N CH ČMe N ČH

described as such (cf Oeconomides, B 19, 2524, Japp, C J 51, 98) Meyer (B 21, 19) proposes to use the name aldine instead of pyrazine CH N CH CH N CH

Other for the group CH N CH or CH N CH

alkyl-pyrazines are formed in like manner by the reduction of the nitroso-derivatives HONCHCOC_nH_{2n+1}, of ketones of the form CH₂COC_nH_{2n+1} As ketine di carboxylic acid does not form an anhydride it has probably the CO₂H C - N CMe

formula rather than CMeN CCO,H

CMe N C CO.H , whence the symmetrical formula CMe N C CO_2H

for ketine given above (Oeconomides)

KETIPIC ACID A name given to DI METHYL-DIKETONE DI-CARBOXYLIC ACID, as it might perhaps

be called di keto adipic acid

KETO This prefix is employed by some chemists to denote the displacement of H2 in the group CCH₂C by O Thus quinone might be called di keto benzene, while aceto acetic acid would be β keto-butyric acid. The prefix 'keto' does not indicate the introduction of a new or game group, whereas the corresponding prefix 'aldehydo-' indicates the introduction of the group CHO, and 'carboxy ' is used to denote the introduction of CO₂H In order to avoid the confusion likely to arise from this circumstance the term 'keto' is avoided in the headings of articles in this Dictionary substances which might have such names given them are described as ketones, quinones, or oxy compounds The prefix kero- has also been used as indicating sub stitution of hydrogen by the ketonic group CO CH₂, thus Erdmann (B 21, 635) terms CH₂ CO C₁₀H₆ OH keto naphthol In keto compounds the group CO CH may often be regarded with equal propriety as C(OH) C, and such compounds are named in accordance with the latter formula Thus phloroglucin may be described as tri-keto-benzene hexahydride or as tri-oxybenzene

DI-KETO- HEPTANE v METHYL BUTYL DI

DI-KETO-HEXANE v METHYL PROPYL DI

a-B-DIKETO-HEXYLENE v METHYL ALLYL-

KETO-HEXA HYDRO-BENZOIC ACID CY ANHYDRIN v Nitrile of Oxy isophthalic acid HEXAHYDRIDE

DI-KETO-HYDRINDENE v INDONAPHTHO-OUTNONE

DI-KETO-INDONAPHTHENE v INDONAPH THOQUINONE

KETO-LACTONIC ACID C,H,O, [1819] When a-acetyl-\$-ethyl-succinic ether is heated it partly breaks up into alcohol and ethyl keto lactonate, which, on saponification, gives potassie ketolactonate (S Young, C J 43, 175, A 216, 45) It is also formed, together with CO.H.CHEt CH.Ac, by boiling the other

(CO, lt.CHEt CHAc CO, Et) with dilute HCl, and may be extracted from the product by ether. The free acid crystallises from water, and is al. sol cold water, m sol hot water

Salts -BaA'22H2O -AgA'

Reaction -1 Heated with baryta the following reaction occurs 2C.H.O.+ 3BaO + H.O The $= 2BaCO_3 + Ba(C_7H_{11}O_3).$ new acid. C,H₁₂O₃, appears to be 'iquid, it forms a very soluble and unstable silver salt —2 Cold baryta produces an unstable dibasic acid, CaH, Oas by

assimilation of H₂O

Constitution — Ketolactonic ether is formed from CO,Et CHAc CHEt CO,Et by splitting off HOEt Inasmuch as CO, Et CMeAc CHEt CO, Et does not form in the same way the ether of a crystalline acid it is probable that the H which is here displaced by methyl goes to form alcohol in the formation of the ketolactoric ether. And since ketolactonic ether appears to be a lactone it should be

CO,Et C CHEt CO,

CH, Ö O-CO.H C CHEt CO the acid being CH, CO --

KETOLE Another name for Indoir (Jackson, B 14, 879)

The ketones, in their simplest KETONES form, contain a carbonyl group CO attached to two monad hydrocarbon radicles If the twa radicles are identical, as in acetone (dimethylketone) CH, CO CH, the compound is a simple ketone, if different, as in methyl ethyl ketone CH, CO CH, CH,, it is a mixed ketone

Just as the fatty acids of the series C, H, O, may be derived from the hypothetical carbonic acid CO(OH), by replacing one hydroxyl group by a monad hydrocarbon radicle, so the ketones may in turn be derived from the fatty acids by replacing the remaining hydroxyl group by a second radicle

HO CO OH Carbonic acid CH, CO OH Acetic acid

«OH, CO CH» Acetone

There is therefore a simple ketone derivable from each fatty acid by the introduction of a hydrocarbon radicle, identical with that which is attached to the carboxyl group of the acid, in place of its hydroxyl group

If one of the radicles in a ketone is hydrogen the resulting compound is an aldehyde

CH, CO H Aldehyde

CH,CO CH, Acetone

and owing to this similarity in constitution, the aldehydes and ketones have many reactions in common In the case of formic acid the radiole attached to carboxyl is hydrogen, and the ketone therefore coincides with the aldehyde

H CO OH

H CO H Formaldehyde.

From this point of view the ketones may be regarded as homologues of formaldehyde

Compounds containing two carbonyl groups are termed deketones, those containing three, triketones

Fatty ketones

Formation.—1 By the destructive distilla-

tion of the calcium salts, o., better still, of the barrum salts, of acids of the series C,H,,O,

(CH₂ CO O)₂Ca = CH₂ CO CH₂ + CaCO₂ If a mixture of the salts of two acids is

employed, a mixed ketone, containing the hydrocarbon radicles of both acids, is formed

 $\begin{array}{c} ({\rm CH_s~CO~O)_sCa} + ({\rm C_sH_s~CO~O)_sCa} \\ = 2{\rm CH_s~CO~C_sH_s} + 2{\rm CacO_s} \\ ({\rm Williamson},~C~J~1852,~^38) \end{array}$

If one of the salts is a formate, an aldehyde is formed, a hy rogen atom from the formate attaching itself to the carbonyl group

(CH, CO O), Ca + (H CO O), Ca = 2CH, CC H + 2CaCO,

(Piria, Cimento, 3, 126, A 100, 104, Limpricht, A 97, 508)

In the preparation of k tones by the de structive distillat on of salts it is advantageous, if the molecular weight of the ketone is high, to conduct the distillation under reduced pressure (Krafft, B 15, 1693)

2 By the destructive distillation of the cal cium compounds of primary alcohols (Destrem, A Ch [5] 27, 7) In this reaction the alcoholates are converted, with evolution of olefins and hydrogen, into salts of fatty acids

 $(\tilde{C}_1H_3O)_2Ca = 2C_2H_4 + \tilde{C}aO + H_2O$

 $(C_1H_2O_2)Ca + 2H_2O = (C_2H_2O_2)Ca + 4H_2$ and the calcium acetate is then decomposed by the heat, yielding acetone A por on of the acetate, however, reacts with the calcium oxide, evolving methane

3 By heating a mixture of the sodium com pound of an alcohol and the sodium salt of a fatty acid in a current of carbon monoxide, mixtures of higher ketones are formed, along with sodium salts of higher organic acids (Geuther, A 202, 288) The constitution of these ketones is not known with certainty, and the process in which they are formed is not understood

4 By the action of acyl chlorides on zinc alkyls (Freund, A 118, 1, cf Pawlow, A 188, 104) The acyl chloride is added to the zinc alkyl, at first gradually, afterwards more rapidly, cooling with ice during the operation The mixture is then decomposed with excess of water

 $CH_1 COCl + Zn(C_2H_3)_2$ = $CH_2 CCl(OZnC_2H_3) C_2H_3$,

 $2CH_{s}$ $CCl(OZnC_{s}H_{s})$ $C_{s}H_{s} + 2H_{s}O$ $= 2CH_{1} CO C_{2}H_{3} + 2C_{2}H_{4} + ZnCl_{2} + Zn(OH)_{2}$

If the mixture is allowed to stand too long be fore adding water, the additive compound formed in the first stage of the process reacts with a second mol of alkyl chloride, exchanging its halogen for alkyl and generating a compound which, on treatment with water, yields a ter tiary alcohol

5 By the oxidation of secondary alcohols $CH_3 CH(OH) CH_3 + O = CH_3 CO CH_3 + H_2O$

6 By the oxidation of secondary acids of the lactic series with potassium bichromate and dilute sulphuric acid Thus hydroxy-isobutyric acid yields acetone

 $(OH_2)_2C(OH)CO_2H + O = (OH_2)_2OO + OO_2 + H_2O$ 7 Certain ketonic acids part with carbon dioxide, forming ketones This decomposition takes place very readily in the case of the Thus when ethylic aceto-8-ketonic acids acetate is warmed with a caustic alkali it is

hydrolysed, and the liberated acid splits off carbon dioxide, thus

CH, CO CH, CO, H = CH, CO CH, + CO, 8 Alcohols containing a hydroxyl-group attached to a doubly-linked carbon-atom do not appear to be capable of existing in the free state, and change, at the moment of their formation, into either aldehydes or ketones, the former transformation occurring when the hydroxyl group is situated at the end of, the latter when it is within, the chain

 CH_2 $CH(OH) = CH_1$ CHOCH, C(OH) CH, = CH, CO CH, (Erlenmeyer, B 13, 809, 14, 320)

9 When secondary or secondary tertiary glycols are treated with dehydrating agents, such as phosphorus pentoxide or zinc chloride, they part with water, forming ketones bably an unsaturated alcohol is first produced, and this changes, at the moment of its forma tion, into a ketone (v preceding paragraph).

CH, CH(OH) CH(OH) CH₁-H₂O

= CH, CH C(OH) CH, = CH, CH, CO CH, Primary glycols, when thus treated, yield aldehydes Tertiary glycols (pinacones) are dehydrated even by boiling with dilute sulphuric acid forming ketones, the reaction being accompanied in this case by the migration of an alkyl group

> $(CH_2)_2C(OH)C(OH)(CH_2)_2-H_2O$ Pinacone

= (CH₂)₃C CO CH₆ Pinacolin

10 When the homologues of acetylene are passed into a solution of mercuric chloride heated to 90°-95° they take up the elements of water, yielding ketones (Kutscherow, B 17, 18) $CH_1 CCH_1 + H_2O = CH_1 COCH_2$

Acetylene itself yields aldehyde

11 Letones, especially acetone, are formed in the destructive distillation of wood, sugar, citric acid, and various other organic compounds

Properties and Reactions -The lower members of the ketone series are liquids, with a peculiar ethereal odour, boiling without decom-The higher homologues, beginning position

with CiaH co, are crystalline solids

The ketones are isomeric with the aldehydes containing the same number of atoms of carbon They closely resemble the aldehydes in many of their reactions, but are distinguished from them by not reducing ammoniacal silver solutions. Like the aldehydes, many of the ketones combine with the hydrogen sulphites of the alkalis to form crystalline double compounds The rule given by Grimm (A 157, 262) that only those ketones combine with hydrogen sodium sulphite which contain the group CH2.CO, holds very generally an exception is propone (di-ethyl ketone) CO(C₂H₃), which forms a double compound, although with difficulty These compounds are used in separating and purifying the ketones on treating the double compound with sodium carbonate the ketone is liberated. The ketones, like the aldehydes, unite with hydrocyanic acid to form nitriles of hydroxy-acids (CH₃)₂CO + HCN = (CH₃)₂C(OH) CN (Urech, A 164, 258, Tiemann a. Friedlande., B 14, 1971) and these nitriles react with ammonia, yielding nitriles of amido-acids (CH₂), C(OH) CN + NH, $=(CH_2)_*C(NH_2)CN+H_2O$ (T a. F.). — In 104 KETONES.

presence of caustic potash, acetone unites with chloroform to form acetone-chloroform (OH2),C(OH) CCl2, which when Leated with water to 180° yields hydroxy-isobutyric acid and hydrochloric acid (Willgerodt, B 14, 2451, 16, 1585) - Sodium amalgam, acting on aqueous solutions of the ketones, reduces them to secondary alcohols, acetone is converted into isopropyl alcohol $(CH_3)_2CO + H_2 = (CH_3)_2CH OH$ (Friedel, CR55, 53) At the same time, a second reaction occurs in which 2 mols of the ketone are united during the process of reduction, forming a tertiary glycol, or pinacone $2(CH_3)_2CO + H_2$ = $(CH_3)_2C(OH) C(OH)(CH_3)_2$ —The ketones are less susceptible of oxidation than the aldehydes, and, unlike the latter, can never yield by oxida tion an acid containing the same number of carbon atoms They are best oxidised by boil ing them with a mixture of potassium bichromate and dilute sulphuric acid Popoff (A 161, 300) has formulated the following rules regarding the products formed in the oxidation of the ketones rules to which, however, there are occasional exceptions The ketone is broken up at a point between the carbonyl group and one of the alkyl groups, the combined carbonyl being oxidised to carboxyl, and the separated alkyl being oxidised, if primary, to a fatty acid with the same number of atoms of carbon as the alkyl itself, and if secondary, to a ketone, which may in turn be further oxidised If a ketone con tains two dissimilar alkyls, the carbonyl group will remain attached to that carbon atom which has most hydrogen combined with it, unless in the case of a tertiary alkyl or a radicle of the benzene series, when the carbonyl group will remain in combination with the non hydro genated carbon atoms If the two dissimilar alkyls are both primary, or both secondary, or both tertiary, the carbonyl will remain attached to the alkyl of lower molecular weight following equations illustrate these rules

 $CH_{2} CO CH_{2} + 3O = CH_{2} CO_{2}H + H CO_{2}H$ $CH_{2} CO CH_{2} \cdot CH_{2} + 3O = CH_{2} CO_{2}H + CH_{2} CO_{2}H.$

> CH₂ CH₂ CH₂ CO CH(CH₂)₂ + 2O = CH₃ CH₂ CH₂ CO₂H + CO(CH₃)₂. CO C(CH₂) + 3O₂H CO H + (CH₃) C C(CH₃) C C C(CH₃) C C(CH₃) C C(CH₃) C C(CH₃) C C(CH₃) C C(CH₃)

 CH_{a} CO $C(CH_{a})_{a} + 3O = H CO_{a}H + (CH_{a})_{a}O CO_{a}H$ CH_{a} CO $C_{a}H_{b} + 8O = H CO_{a}H + C_{a}H_{b} CO_{a}H$

In several cases, however, a subordinate reaction, in which the ketone is oxidised in a way the reverse of that predicted by the rule, occurs simultaneously—Chlorine and bromine give substitution compounds—Phosphorus pentachloride replaces the oxygen of ketones by two chlorine atoms—Ammonia reacts less readily with ketones than with aldehydes With acetone it forms diacetonamine C₂H₁₂NO, and triacetonamine C₂H₁₂NO—With hydroxylamine in aque ous solution the ketones yield the ketoximes.

OH₂ CO CH₂ + NH₂ OH = OH₂ C(N OH) CH₃ + H₂O. Acetoxime

The ketoxime, are generally solid crystalline compounds, volatile without decomposition Concentrated hydrochloric soid decomposes them into hydroxylamine and ketone.—In like

manner phenylhydrasine reacts with the ketones, eliminating water and forming ketohydrazones: CH₂ CO.CH₂ + O.H., NH NH₂

= CH₃ C(N NHC₆H₅) CH₃ + H₂O
Acetonephenylhydrasone

The ketohydrazones of the fatty series are for the most part oily liquids, which may be distilled under reduced pressure. Acids decompose them into phenylhydrazine and ketones (E. Fischer, B. 16, 661)—Nitrous acid converts the ketones into isonitroso ketones. The reaction occurs more readily, however, with ethereal salts of n trous acid, thus when a mixture of amyl nitrite and acetone is warmed with hydrochloric acid isonitroso acetone is formed.

CH_a CO CH_a + C_bH , O NO

= CH, CO CH N OH + C,H, OH

Sodium ethoxide may be substituted for hydro chloric acid in the foregoing reaction, but in this case the sodium compound of the isonitroso ketone is formed and must afterwards be decomposed by acetic acid (Claisen, B 20, 252, and 656, Claisen a Manasse, B 20, 2194) The isonitroso ketones are also readily obtained by the action of nitrous acid on aceto acetic acid and its homologues

CH₃ CO CH₂ CO₂H + HNO₃ Aceto acetic acid

- CH₂ CO CH N OH + CO₂ + H₂O Isonitroso-acetone

(V Meyer a Zublin, B 11, 695, Ceresole, B 15, 1328)—Concentrated nitric acid converts the ketones into dinitro paraffins thus propione CH₂ CH₂.CO CH₂ CH₃ yields dinitroethane CH₂ CH(NO₂)₂ (Chancel, Bl 31, 504)—The ketones react with the mercaptans, eliminating water and yielding 'mercaptoles' (thioketates), ethyl thiodimethylketate is formed when gaseous hydrochloric acid is passed into a mixture of acetone and mercaptan

 $(CH_1)_2CO + 2C_2H_3$ $SH = (CH_2)_2C(SC_2H_3)_2 + H_2O$ (Baumann, B 18, 887) The mercaptoles are liquids, insoluble in water, not volatile without decomposition, stable towards alkalis and dilute acids - Under the influence of dehydrating agents, such as sulphuric acid, zinc chloride, hydrochloric acid, &c, the ketones readily undergo condensation, two or more molecules combining, with elimination of water, to form more Thus 2 mols of acetone complex compounds unite to form mesityl oxide (CH,),C CH CO CH,, and 3 mols to form either phorone (CH₃)₂C CH CO CH C(CH₃)₂ or mest ylene (1, 3, 5 trimethylbenzene) C₈H₁(CH₃)₃, according as 2 or 3 mols of water are eliminated in the

Bensene ketones Ketones of this class may either contain two benzene radicles directly attached to carbonyl, as in benzophenone (diphenyl ketone) C_aH_a CO C_aH_a, or the carbonyl group may unite a benzene redicle and a fatty radicle, as in acetophenone (phenyl niethyl-ketone) C_aH_a CO CH_a, or one or both of the benzene radicles may be attached to carbonyl by means of a fatty group, as in phenyl benzyl-ketone C_aH_a CO CH_a C_aC_aH_a, or di benzyl ketone C_aH_a CO CH_a C_aC_aH_a, or di benzyl ketone C_aH_a CO CH_a C_aC_aH_a.

C.H. CH. CO CH. O.H.

Preparation — Many of the methods already
described for the preparation of the fatty ketones
are also applicable in the case of the benzene

ketones Thus benzophenone may be obtained by the distillation of a benzoate

(C_sH_s CO O)₃ = (C_sH_s)₂CO + CaCO₂, and acetophenone by distilling a mixture of a benzoate and an acetate

(O₂H₂ CO O)₂Ca + (CH₂ CO O)₂Ca = 2C₂H₃ CO CH₂ + 2CaCO₃ Again, acetophenone may be obtained by the action of benzoyl chloride on zinc methyl, but if it is desired to introduce a benzene radicle in place of the haiogen of the acyl chloride the mercury compound of that radicle must be em ployed C_0H_a $COCl + H_a(C_0H_a)_2$ = $(C_0H_a)_2CO + H_g(C_0H_a)Cl$

The benzene retones are also formed, like the fatty ketones, by the oxidation of the correspond ing secondary alcohols

$$(C H_s)_2CH OH + O = (C_6H_s)_2CO + H_2O$$
, Diphenylcarbinol

and of secondary glycolic acids containing benzene radicles

$$(C_0H_0)_2C(OH)CO_2H + O$$

Bensilio acid $=(C.1)$

 $= (C_4H_1),CO + CO_4 + H_4O_4$

further, by splitting off carbon dioxide from ketonic acids of the benzene series

$$C_eH_s$$
 CO CH_z CO₂ $H = C_eH_s$ CO $CH_s + CO_2$
Benzoylacetic acid

By shaking phenylacetylene with sulphuric acid of 75 pc it takes up the elements of water, yielding acetophenone

 C_8H_3 \bar{C} $CH + H_2O = C_uH_a$ CO CH_a (Friedel a Balsohn, Bl [2] 35, 55)

The following modes of formation are pe culiar to benzene ketones -

1 By the action of an acyl chloride on a benzene hydrocarbon in presence of aluminium chloride CH, COCl + C,H, = CH, CO C,H, + HCl (Friedel a Crafts, A Ch [6] 1, 507) In this reaction the acid radicle always attaches itself to a benzene nucleus, and never to a fatty group In like manner ketones containing two benzene radicles directly united to carbonyl may be prepared by acting on a benzene hydrocarbon with carbonyl chloride in presence of aluminium

chloride $COCl_2 + 2C_6H_6 = CO(C_6H_3)_2 + 2HCl$ 2 The last mentioned class of ketones may also be obtained by heating a mixture of a benzene carboxylic acid and a benzene hydro

carbon with phosphorus pentoxide

 C_aH_a CC OH + C_aH_a = C_aH_a CO C_aH_a + H_aO 8 By the oxidation of hydrocarbons in which two benzene radicles are united by a methylene group

 C_aH_a CH_a $C_aH_a + O_a = C_aH_a$ CO $C_aH_a + H_aO$ Ketone-alcohols are obtained by polymerising benzene aldehydes with potassium cyanide

Ketone phenois are formed when acyl chlor ides of the benzene series act on phenols in presence of zinc

$$C_eH_a$$
. $COCl + C_oH_a$ $OH = C_eH_a$ COC_eH_a $OH + HCl$

p-Hydroxybensorbenone

The acid radicle enters the nucleus of the phenol in the para- position to the hydroxyl group

Properties and Reactions — The benzene ketones are liquids and solids, boiling without decomposition and having a pleasant aromatic odour

In most of their reactions they closely re semble the fatty ketones Popoff's rules (v supra) apply to the oxidation of the benzene the carbonyl group always remains ketones attached to a benzene nucleus to which it is directly united Like the fatty ketones, the benzene ketones react with hydroxylamine and with phenyl-hydrazine eliminating water and yielding hydroximes and hydrazones On reduction with sodium amalgam they form secondary alcohols, but heating with hydriodic acid, or distillation with zinc dust, reduces them to the corresponding hydrocarbons

$$(C_6H_3)_2CO + 2H_2 = (C_6H_5)_2CH_2 + H_2O$$

Diphenylmethane

By fusion with caustic alkalis they yield a salt of a benzene acid together with a hydrocarbon

 $C_eH_s CO C_eH_s + KOH = C_eH_s CO_2K + C_eH_e$ They are less subject than the fatty ketones to undergo condensation with elimination of water, and those which contain two benzene radicles directly attached to the carbonyl group do not exhibit this tendency at all

Only those benzene ketones combine with hydrogen sodium sulphite in which the carbonyl is attached to two fatty groups, one of which is methyl thus, benzyl methyl ketone C₆H₃CH₂CO CH, and methyl phenylethyl ketone C₆H₃CH₂CO CH, CO CH, form double compounds, acetophenone C₆H₃CO CH, does not Diketones The diketones contain two car-

bonyl groups attached to hydrocarbon radicles If the two carbonyl groups are directly united, the compound is an a diketone, if they are united by a carbon atom, it is a \$-diketone. if by a chain of two carbon atoms, a γ-ketone, and so on

Some of the diletones, such as benzil C_eH_s CO CO C_sH_s , have been known for a considerable time, but the majority are of recent discovery Their chief interest lies in the ease with which the two carbonyl groups may be made to condense with one or more molecules of some other substance to form closed chain compounds In this way glyoxalines, quinolines, pyrazoles, furfurans, pyrrholes, thiophens, and similar compounds have been prepared

These may be regarded as a-Diketones homologues of the dialdehyde glyoxal, CHO CHO They may be obtained by the action of chlorine, or, better, of nitric acid, on a ketone alcohols

(Laurent, A Ch. [2] 59, 402, Zinin, A 34, 188) By hydrolysing the isonitrosoketones by boiling them with dilute sulphuric acid

Von Pechmann, B. 21, 1411)

The benzenoid a diketones react with caustic potash to form secondary glycolic acids, the two 106 KETONES.

hydrocarbon radicles attaching themselves to the same carbon atom

$$\begin{array}{c} \mathbf{C_{e}H_{5}} \text{ CO CO } \mathbf{C_{e}H_{5}} + \mathbf{KOH} = (\mathbf{C_{e}H_{5}})_{2}\mathbf{C(OH)} \text{ CO}_{2}\mathbf{K} \\ \text{Potassium benzilate} \\ \text{(diphenylglyoolate)} \end{array}$$

(Liebig, A 25, 25, Zinin, A 31, 329) In like manner glyoxal yields glycolic acid. The fatty adiketones, however, condense to form quinones $(q \ v)$ —a-Diketones react with 2 mols of hydroxylamine to form dihydroximes. Benzil dihydroxime is remarkable as occurring in three isomeric modifications, all of the formula C_sH_5 C(N OH) C(N OH) C_sH_5 , an isomerism which is explained by Victor Meyer by means of tridimensional formulæ (Auwers a V Meyer, B 22, 705, cf also Hantzsch a Werner, B 23, 11) These three hydroximes, when heated, part with water, yielding in each case the same closed-chain compound—an anhydride

(Auwers a V Meyer, B 21, 810) —With odiamines the a-diketones yield quinoxalines (azines)

(Hinsberg, B 17, 322, cf Witt, B 19, 915) For an account of the behaviour of a diketones with aldehydes and ammonia v vol 1 p 465

The lowest member of this β-Drketones series which is a true diketone and not a dialdehyde is acetyl acetone CH, CO CH, CO CH, By the action of aluminium chloride on acetyl chloride a crystalline substance of the formula C₁₂H₁₄O₆Al₂Cl₈ is formed, which, on treatment with water, evolves carbon dioxide and yields acetyl acetone (Combes, C R 103, 814) general method for the preparation of β diketones consists in acting on a mixture of a fatty or a benzene fatty ketone and the ethyl salt of a carboxylic acid with sodium ethoxide latter substance produces condensation between the ethereal salt and the ketone with elimination of alcohol

In reality it is the sodium compound of benzoylacetone G_0H_0 CO CHNa CO G_0H_0 which is formed, and it is necessary to decompose this compound with earbon dioxide in order to obtain the free diketone (Claisen, B=20, 655) Di acyl derivatives of acetic acid are decomposed on boiling with water, eliminating water and generating B diketones

$$(C_6H_5 CO)_2CH CO_2H = (C_6H_5 CO)_2CH_2 + CC_2$$

Dibensoylacetic acid Dibenzoylmethane

(Baeyer a W H Perkin, jun, B 16, 2128, E. Fischer a Kuzel, B 16, 2239)

The methylene group in the β-diketones is attached to two electro negative carbonyl groups.

For this reason one atom of hydrogen in this group, like the hydrogen in the methylene group of aceto acetic ether or malonic ether, is replaceable by an alkali metal when presented to it in the form of an ethoxide. By treating the alkali compound thus obtained with the halogen compound of an alkyl or acid radicle, the radicle can be introduced in place of the alkali metal.

The \$\beta\$-diketones react with 1 mol of phenyl hydrazine eliminating 2 mols of water, and forming pyrazoles

(Knorr, B 20, 1104)—Antine reacts with β-diketones in two stages thus when benzoylacetone is heated with aniline at 150° the two substances first unite, parting with 1 mol of water C₄H₃ CO CH₂ CO CH₃ + C₄H₃ NH₂ = C₄H₃ CO CH₂C(N C₄H₃) CH₃ + H₂O, and when the compound thus obtained is heated with concentrated sulphuric acid, it parts with a second mol of water, forming a quinoline derivative

(C Beyer, B 20, 1770) This is a general method for the preparation of quinolines containing alkyls in the α γ positions

γ-Diketones—In these compounds the two carbonyl groups are united by an ethylene radicle The lowest member of the series, acetonyl acetone, was obtained by Paal (B 18, 58) by heating pyrotritaric acid with water at 150°-160°

= CH₂ CO CH₂ CO CH₂ + CO₂ Acetophenone acetone is obtained by heating acetophenone aceto acetic acid (prepared by acing with bromacetophenone on sodaceto acetic ether, and hydrolysing the ether thus formed)

CH, CO CH CH, CO C,H,

2865)

By treatment with dehydrating agents, such as fuming hydrochloric acid or acetic anhy-

KOSIN. 107

inde, the y-diketones are converted into fui turans It is supposed that in this reaction the liketone first forms a 'labile' modification con saining two hydroxyl groups, and that this then parts with water to form the furfuran

Phenylmethyl furfuran

(Paal, B 17, 2756) An unsaturated ketone someric with phenylmethylfurfuran is formed at the same time -Phosphorus pentasulphide converts y diketones into thiophens, whilst with ammonia they yield pyrroles, the reaction in both cases being supposed to be preceded by the above-mentioned transformation of the diketone into its 'labile' modification

C CH, + NH, C CH₃ + 2H₂O

Phenylmethylpyrrole

(Paal, B 18, 367)

An unsaturated y diketone, anhydracetophenonebenz' (aß dibenzoylstyrolene) is formed by the action of caustic potash on a mixture of benzil and acetophenone

Quinones If the two carbonyl groups of a diketone occur in a closed chain of six carbon atoms, the resulting compound belongs to the This group of diketones class of the quinones will be treated of separately (v Quinones).

Triketones A triketone in which the three carbonyl groups are directly united has been obtained in the following manner (von Pechmann, B. 22, 852). Dibenzoylbromomethane

C.H. CO CHBr CO C.H. (prepared by the action of bromine or dibenzoylmethane, v supra) is converted by treatment with potassium acetate the acetate of dıbenzoylcarbınol C_sH_s CO CH(OC₂H_sO) CO C_sH_s, which, when brominated, yields CaH, CO CBr(OC2H,O) CO CaH, When this compound is heated above its meltingpoint (101 5°) it breaks up into acetyl bromide and diphenyltriketone

C,H, CO CBr(OC2H,O) CO C,H,

= C₂H₃OBr + C₅H₅CO CO CO C₆H₅ Diphenyltriketone, like some other compounds in which a carbonyl-group is situated between two electro negative groups, unites with 1 mol of water to form a hydrate, this has probably the constitution C₆H₅ CO C(OH), CO C₆H₅

The formation of another triketone, tribenzoyl methane, in which the three carbonyl groups are attached to the same carbon atom, has already FBJ been referred to

DIKETO-PENTANE v METHYL ETHYL DIKE-

αβ DIKETO-PROPYL-BENZENE v PHENYL-METHYL DIKETONE

KINIC ACID Synonym of Quinic acid

KINO The dried juice, obtained from incisions in the trunk of Pterocarpus marsupium (Mala The name has also been given to the dried juice from other trees, e g Eucalyptus resimfera (Australia) Pterocarpus erinaceus, and Cocco loba uvifera (America) Kino greatly resembles catechu, and is used in dyeing and in medicine It occurs in small brittle opaque reddish black fragments, partly soluble in water, almost entirely soluble in alcohol, insoluble in ether has no odour, but a very astringent taste Used in medicine as an astringent. It gives off pyro catechin when distilled (Eissfeld, A 92, 101) Potash fusion forms phloroglucin and protoca technic acid (Hlasiwetz, A 134, 122, Stenhouse, A 177, 187) Kino contains kinoïn and kino red and other bodies Kinoïn has been described as a 'tannın' (Bergholz, cf Etti, B 17, 2241)

Kinoin C_{1,}H_{1,}O₆ Occurs together with kinored, &c, in gum kino, from which it is extracted by first boiling with dilute HCl, and then ex tracting the solution with ether, yield 11 pc (Etti, B 11, 1879) Colourless prisms Sl sol cold, readily sol hot, water On heating to 120° it gives kino red (C₂₈H₂₂O₁₁) On heating with HCl to 130° it is decomposed into methyl chloride, pyrocatechin, and gallic acid

[160°-170°] Kino red C28H22O11 resin occurring in kino and left undissolved when it is boiled with dilute HCl It is also formed by heating kinoin It is also water, v It is also sol alcohol FeCl, gives a dirty green colouration It dissolves in alkalis It ppts a solution of On fusion it yields a red amorphous anhydride C₂₈H₂₈O₁₀, which also ppts a solution of gelatin The anhydride is also formed by heating kino-red with dilute HClAq. Kino-red yields phenol and pyrocatechin when distilled

KOSIN C₃₁H₃₂O₁₀ [142°] Obtained from cusso or kousso, the dried flowers of the Abyssinian koso tree (Hagenia Abyssinica), used by the inhabitants as a remedy again it tape worm (Flückiger a Buri, Ar Ph [8] 5, 193, Ph. [8] The anthelmintic properties of koso seem to be due to kosin. Sulphur yellow tri metric crystals. Nearly insol. water, v sol

108 KOSIN.

alcohol, ether, benzene, CS2, chloroform, and HOAc. Dissolves in aqueous alkalis and Na2CO3, and is reppd by acids FeCl, colours its alcoholic solution permanently red Cone H₂SO, does not decompose it at 15°, but on warming it forms isobutyric acid and a red amorphous body CasHa, O10 (?) Potash fusion gives formic, butyrio, and oxalic acids Sodium amalgam yields a volatile oil C₃₃H₄₆O₃ and an amorphous yellow substance (C₄H₄O₂).

Acetyl derivative C, H,2Ac,O,e. From kosin and Ac.O

KOUMISS v Milk KYANETHINE v CYANETHINE KYANPHENINE v CYAPHENINE KYANPROPINE v CYANPROPINE

KYNURENIC ACID v OXY QUINOLINE CAB BOXYLIC ACID

KYNURIC ACID v CYNURIC ACID KYNURIN v OXY QUINOLINE

\mathbf{L}

LABURNINE An alkaloid said to occur along with cytisine in laburnum seeds (Huse mann a Marmé, Z [2] 1, 161, 5, 677) crystalline groups of monoclinic prisms, v sol water, sl sol alcohol, nearly insol ether

LAC A substance surrounding the eggs of Coccus laccæ on the twigs of various trees in Bengal and Sumatra These twigs are called stick lac The lac is removed by melting and squeezing through canvas, when the hardened drops are known as seed lac After bleaching by chlorine or charcoal and making into sticks it is known as shell lac or shellac Lac is used for making sealing wax, varnishes, and a red dye called lac dye Lac contains 68 to 88 p c resin (about half of which is soluble in ether), a small quantity of wax and of a red dye, and a larger quantity of a substance insoluble in alcohol The wax [60°] contains ceryl and myricyl alcohols and their stearic, palmitic, and oleic ethers (Benedikt a Ulzer, M 9, 579) Shellac may be freed from wax by dissolving in boiling dilute Na₂CO₂, filtering, and ppg with HCl the boiling be continued too long, liquid shellac 18 produced Shellac freed from wax gives azelaic acid when oxidised by KMnO, (Benedikt a Ehrlich, M 9, 163)

Liquid shellac C₄₈H₇₂O₁₂ Formed by boiling shellac (1,000 g) with NaOH (300 g) and water (20,000g) for 2 hours When cold, sulphuric acid is added and the liquid shaken with ether (B a E) Thick liquid, insol water, v sol alcohol and ether Forms salts with Pb, Ag, Zn, Ba, and Ca — C46H70Mg2O18 amorphous, v sol water, ppd on heating, but redissolves on

Laccaic acid $O_{10}H_{12}O_{0}$ (?) Obtained from lac dye by treating with HClAq, filtering, boiling the residue with water, ppg the solution with lead acetate, and decomposing the pp with H₂S (R E Schmidt, B 20, 1285) Brownish red powder composed of minute tables (from alcohol ether), m sol alcohol, sl sol water, nearly insol ether, insol benzene Decomposes, without previous fusion, at about 180° Alkalis form a crimson solution which has an absorption spectrum like that of carminic acid Baryta gives a violet pp
FeSO₄ a black pp FeCl₂ a black colouration
only It reduces ammoniacal AgNO₂ bu. not
Fehling's solution Cone HNO₂ yields pieric
and oxalic acids Cone HClAq at 180° forms a
substance C₂ H₁₈O₁ Laccasic acid dyes like carminic acid, but its solution in H.SO, shows a different absorption spectrum —K,C,sH,O, (dried

at 100°) flocculent pp formed by adding also holic potash to an alcoholic solution c' the salt BaC_{1s}H_{1s}O_s brownish red pp formed by adding NH₂ and BaCl₂.

LACMOID

Preparation -1 A mixture of resorcinol (20 pts), sodium nitrite (1 pt), and water (1 pt) is slowly heated to 110°, at which temperature a vigorous reaction sets in, the melt is then kept at 115°-120° till it has become quite blue and the evolution of NH₂ has ceased (Traub a Hock, B 17, 2615) -2 By the action of H₂O₂ on am moniacal resorcin solution (Wurster, B 20, 2938) -8 By fusing resorcin (15 g) with KNO2 (18 g) (Benedikt a Julius, M 5, 534)

Properties —Glistening brown powder It is easily soluble in methyl, ethyl, and amyl al cohols, acetone, acetic acid, and phenol, less easily in ether and water, insoluble in benzene and petroleum spirit It dissolves in strong HCl or H₂SO₄ with a blue colour It decomposes below

200°

Lacmoid differs from litmin, the colouring matter of litmus, in being soluble in strong Litmin is insoluble in strong alcohol, though soluble in dilute (50 pc) spirit The solution of litmin in 50 pc alcohol is bleached after a time, while that of lacinoid retains its colour for months The absorption spectra of the two substances do not differ markedly (Hart

ley, R Dublin Soc 5, 159)

LACTAM The anhydride of an amido acid $R''(NH_2)(CO_2H)$ containing the group R'' < CO > NH

(Baever, B 15, 2102)

LACTAMIC ACID IS a AMIDO PROPIONIC ACID Di lactamic acid 18 a IMIDO DI PROPIONIC ACID LACTAMIDE v Amide of LACTIC ACID

LACTARIC ACID C₁₃H₃₀O_r Prepared by pressing the juice out of the mushroom (Lactarius piperatus) and extracting the residue with ether or boiling alcohol (Chuit, Bl [3] 2, 158) White leaflets (from alcohol), v sol hot alcohol, ether, CHCl₂, CS₂, and benzene, v sl sol cold alcohol and petroleum spirit, insol water

Salts -NaA' greasy scales, decomposing at 250°-KA' silvery scales, decomposing at 245° without meltin.g.—KHA', silky scales. [115°]—NH₄A' [92°], white leaflets, decomposed by boiling water —CaA'₂ scales When distilled it forms the ketone (O₁,H₂₀),CO [82°]. BaA', white amorphous pp Insol water, alcohol, and ether -Pb.HA'. [114°]. Thin transparent leaflets.

Methyl ether MeA' [J8°] White scales Sol. ligroin and ether

Ethyl ether Eth' [36°] White scales V sol warm alcohol, ether, chloroform, and CS₂ Amide C₁₂H₁₈O NH₂ [108°] Trimetric needles

LACTIC ACID C₂H₂O, te CH₂CH(OH) CO₂H₃COxy propionic acid Ethyledene lactic acid Fermentation lactic acid Mol w 90 S G 29 1 2403 (Bruhl), 19 1 2485 (Mendeléeff, C R 50, 52) $\mu_{\rm S} = 1\,4469$ R_{$_{\rm C}$ 0 = 31 18}

Isomerides — Lactic acid is isomeric with hydracrylic acid, and appears to be chemically identical with sarcolactic acid (v infra)

In 1863 Wislicenus got from ethylene chlorhydrin and KCN, by saponifying the product, a lactic acid which formed a cr-stalline zinc salt ZnA', 2aq He called it ethylene lactic acid, thought it was identical with Liebig's sarco lactic acid (A 128, 4) Dossios (A 146, 168) said that sarcolactic acid gave, on oxidation, Wishcenus held (A 167, 346) malonie acid that his ethylene lactic acid was not hydracrylic acid, for by the action of HI he was unable to obtain \$ 10do propionic acid He said also that his ethylene sactic acid differed from sarcolactic, although it accompanied sarcolactic acid in extract of meat Erlenmeyer (A 191, 261) showed that Wislicenus's ethylene lactic acid from glycol chlorhydrin is hydracrylic acid, and could be converted by HI into \$ 10do propionic acid The acid accompanying sarcolactic acid 18, according to Siegfried (B 22, 2711) the acetyl

derivative of lactic acid

Occurrence -1 Discovered by Scheele in sour milk and first recognised as a peculiar acid by Berzelius -2 In opium (Smith, Ph [2] 7, 50, Buchanan, B 3, 182)

Formation -1 by the lactic fermentation of milk sugar, cane sugar, or glucose (v Fermentation, vol in p 543) -2 By the exidation of propylene glycol by the oxygen of the air in presence of platinum black (Wurtz, A 105, 206, 107, 192) —3 By boiling a chloro propionic acid with water and Ag₂O (Wurtz, A Ch [3] 59, 165, Buff, A 140, 156) In like manner from a bromo propionic acid (Friedel a Ma chuca, A 120, 286) -4 By the action of nitrous acid upon alanine (Strecker, A 75, 27, 42) -5 By the reduction of pyruvic acid by sodium amalgam (Wislicenus, A 126, 227) or with zinc in presence of dilute acetic acid (Debus, C J 16, 260) -6 From aldehyde by combination with HCy a d saponification of the resulting nitrile (Wishcenus, A. 128, 6, Simpson a Gautier, A. 146, 254) —7 By heating di chloroacetone with a large quantity of water at 200° (Linnemann a Zotta, A 159, 247) -8 By boiling glucose with aqueous NaOH (Hoppe Seyler, B 4, 346) —9 When glucose (20 g) is allowed to stand with potash (40 g) and water (200 c c) at 40° in a flask loosely plugged with cotton wool, it is converted within 24 hours into lactic soid (8g) and another soid, soluble in alcohol (Nencki a Sieber, J pr 183, 499) Lactic acid may possibly be thus formed in animals from sugar The decomposition occurs even in very dilute solutions, thus even 9 g of glucose and 9g of potash dissolved in 8 litres of water and kept at 85°-40° are converted in 10 days into potassium lactate Na₂CO₂ does not decompose

sugar at 40°, nor does NH_s, but NaOH_t NMe_tOH and neurine do convert it into lactic acid. Creatiline and guanidine produce no lactic acid. Milk sugar and maltose behave like glucose. Lactic acid is formed when glucose (dextrose) (1 pt), water (10 pts) and KOH (2 pts) are left, even in an atmosphere of hy drogen, for 48 hours at 35° No sugar is left (Nencki a Sieber, J pr [2] 26, 1, Kiliani, B 15, 701)—10 By heating cane sugar with baryta at 150° (Schutzenberger, Bl [2] 25, 289)—11 Among the products of the distillation of glycerin with KOH (Herter, B 11, 1167), and formed, together with formic and oxalic acids, by boiling glycerin with potash solution (Debus, A 109, 229)

The filtered solution of Preparation -1 sour whey evaporated nearly to dryness, in strong alcohol, is mixed with alcoholic tartaric acid, as long as any precipitate of tartrate of potassium, sodium, and calcium is formed, the liquid decanted after 24 hours, and evaporated. the residue dissolved in water, the solution digested with carbonate of lead, till lead dissolves in it, the filtrate evaporated, neutralised with carbonate of barium, again filtered, and diluted with water, the whole of the barium precipitated with sulphate of zinc, and the fil trate evaporated till lactate of zinc crystallises out (Berzelius, Lehrb Ausg 5, v 241) -2 Three kilos of cane sugar and 15 g of tartario acid (which serves to invert the cane sugar) are dissolved in 13 kilos of boiling water. 11 kilos of levigated chalk added after two days, together with 60 g of stinking cheese, suspended in 4 kilos of sour milk (decaying cheese favours the production of lactic acid and retards its conversion into butyric acid), the mixture set aside at a temperature between 30° and 35°, and well stirred every day till, in the course of six or eight days, it is converted into a stiff paste of lactate of calcium, this paste is boiled for an hour with 15 g of quicklime and 10 kilos of water, the solution strained through a cloth filter and evaporated to a syrup, the crystalline mass, which forms in four days, pressed, first by itself, then three or four times, after having been each time stirred up, with 14 of its weight of cold water, and the lactate of calcium thus purified is dissolved in twice its weight of boiling water. To the solution of every 32 pts of the calcium salt there is then added a mixture of 7 pts oil of vitriol and 7 pts water, the lactic acid, while still hot, is strained through linen to separate it from sulphate of lime, the filtrate obtained from 7 pts of oil of vitriol is boiled with 12 pts carbonate of zinc for a quarter of an hour (by longer boiling a very sparingly soluble basic salt is formed), the liquid is filtered boiling hot, the colourless crystalline grains of lactate of zinc, which separate on cooling, are freed from sulphuric acid by washing with cold water, and additional quantities of crystalline grains are obtained by evaporating the mother-liquor almost to the end Lastly, 1 pt of the zinc palt is dissolved in 7½ pts of boiling water, sulphuretted hydrogen passed through the solution as long as sulphide of kine is precipitated, and the filtrate boiled and evaporated on the water bath to a syrup, whereupon 8 pts. of the sine salt yield 5 pts. of syrupy lactic

acid (Bensch, A 61, 174) By this process, 100 pts of cane sugar yield 117 pts of lactate of calcium, which, if the sugar was white, is colourless, and does not require to be purified by pressure (cf Engelhardt a Maddrell, A 63, 83, 70, 241, Boutron a Fremy, J Ph 27, 341) 8 Lautemann (A 113, 242) recommends the following modification of Bensch's process of preparation -Retaining the proportions of sugar, tartaric acid, milk, and cheese indicated by the latter, he takes one third more water, uses 1,200 g oxide of zinc (commercial zinc white) instead of levigated chalk, and keeps the temperature as constantly as possible between 40° and 45° during the fermentation eight or ten days, the inside of the vessel is lined with white crystals of lactate of zinc, which can be obtained pure by one or two crystalli sations from boiling water The lactic acid prepared from the zinc salt generally contains mannite, which does not completely crystallise out from the concentrated and To separate this, the aqueous acid is shaken up with ether. and then the ethereal layer is pipetted off and evaporated it then leaves pure lactic acid -4 The following mixture is recommended by C O Harz (Vierteljahrsschrift pr Pharm 20, 501), 3 pts milk sugar, 36 pts ordinary water, 05 to 075 pt flour containing a large proportion of gluten, a little beer yeast, 6 pts of soda crystals, or 3 pts of sodium bicarbonate When the fermentation has once been set up by milk sugar, it may be continued by addition of cane sugar -5 By the action of NaOH or KOH on dextrose or levulose, the operation being per formed as follows -A solution of 500 grms of cane sugar in 250 cc of water and 10 cc dilute sulphuric acid (3 pts H2SO, to 4 pts H2O) is heated to 50° in a closed vessel for 3 hrs After cooling, 400 cc of aqueous NaOH (50 pc) is slowly added The mixture is then warmed to 60°-70° till it no longer reduces Fehling's solu tion, the calculated quantity of H2SO4 (same strength as b fore) is then added, and the Na, SO, made to crystallise out by cooling and The mass is extracted with 93 pc agitation spirit and filtered, the filtrate is divided into two portions, one half being neutralised with ZnCO3 filtered hot and the other half added On cool ing, the zinc lactate crystallises out in a nearly pure state, the yield is 200 grms (Kiliani, B 15, 699, cf Hoppe Seyler, B 4, 346)

Properties — Colourless syrup with very sour taste Hygroscopic Miscible with water and alcohol, sl sol, ether Does not solidify at -24°

Reactions—1 When gradually heated it gives off water at 130° leaving sold lactide. At 250° to 300° the products are CO, CO₂, alde hyde, and lactide—2 Dilute H₂SO₄ at 130° gives aldehyde and formic acid (Erlenmeyer, Z 1868, 343) CH₂ CH(OH) CO₂H = CH₂ CHO + HOO₂H. 3 When gently heated with cone H₂SO₄ it gives off CO freely (Pelouze, A Ch [3] 13, 257)—4 Boiling nitric acid forms oxalio acid—5 Dis tillation with NaCl, dilute H₂SO₄, and MnO₂ yields aldehyde and chloral (Stadeler, A 69, 382)—6 Pistillation with MnO₂ and dilute H₂SO₄ yields aldehyde and CO₂—7 Fuming H₂SO₄ gives methane disulphonic acid (Strecker, A. 118, 291)—8 Chromic acid sinches gives

acetic acid and CO₂ (Chapman a Smith, Z. 367, 477)—9 KMnO₄ gives pyruvic acid—10 PCl, acting on dry calcium lactate gives chloro-propionyl chloride CH₂ CHCl COCl whence water forms a chloro propionic acid 11 HIAq reduces it to propionic acid (Lautemann, A 113, 217) —12 A concentrated solu tion of potassium lactate submitted to electrolysis yields aldehyde and CO₂ (Kolbe, A 118, 244, Brester, Z 1666, 680)—13 Distillation with quicklime yields alcohol $C_3H_0O_3$ = $CO_2 + C_2H_0O$ (Hanriot, C R 101, 1156, Bl[2] 45, 80) —14 Heated at 170° in a stream of gaseous HBr, or at 100° in sealed tubes with conc HBrAq, it yields a bromo propionic acid (Kekulé, A 130, 11) -15 Bromine at 100° decomposes lactic acid (Beilstein, A 120, 227) Br acting on an ethereal solution of lactic acid forms tribromo pyruvic ether (Wichelhaus, A 143, 10, Klimenko, J R 8, 125) -16 The d y distillation of calcium lactate produces CO, ethylene, propylene (Gossin, Bl [2] 43, 49), acrylic acid, phenol (?) (Claus, A 136, 287), and other products—17 Distillation of calcium lactate with soda lime yields acetic, propionic, butyric, hexoic, and other fatty acids Heating calcium lactate with KOH at 280° yields formic, acetic, propionic, butyric, and oxalic acids (Hoppe Seyler, H 3, 352)—18 Among the products of the nutrefactive fermentation of calcium lactate are hydrogen, CO2, acetic, propionic, butyric, and n valeric acids and ethyl alcohol (Pasteur, Bl 1862, 52, Strecker, A 92, 80, Fitz, B 11, 1898, 12, 479, 13, 1309)—19
Heating with mamido benzoic acid forms CH, CH(OH) CO NH C₆H, CO₂H crystallising from water in small prisms [162°] (Pellizzari, A 232, 154), which at 240 forms an anhydride CH, CH

N C_oH₄ CO₂H [243°] The corre

sponding acetyl derivative

CH₃ CH(OAc) CO NH C₆H₄ CO₂H melts at 148° Estimation —The substance, acidified with H₂SO₄, is extracted with ether, the ethereal solution evaporated, the residue treated with water and the aqueous solution ppd with lead acetate and filtered The filtrate is then ppd with alcoholic NH₄, and the pp of Pb₂O₂2(C₅H₆O₂) washed with alcohol, dried, weighed, ignited, and weighed again (Palm. Fr 26, 33)

Salts -The crystalline lactates do not effloresce in the air, but give off water in vacuo They are not decomposed at 150° They are insoluble in ether and, for the most part, spar ingly soluble in cold water —Ammonium salt forms deliquescent prisms, and gives off NH, when exposed to air -NaA' (at 140°) amor phous, deliquescent mass, v sol water and alcohol, ppd by ether from its alcoholic solution —Na₂C₃H₄O₂ te CH₃ CH(ONa) CO₂Na ob tained by the action of sodium on the preceding at 130°. Hard, deliquescens brittle mass. De composed by cold water, with evolution of heat, into NaOH and NaC,H,O, Absorbs CO, from the air, forming 1,a,CO, and sodic lactate Basic sodium lactate appears to dissolve without decomposition in perfectly dry alcohol MeI it gives Nal and CH, CH(OMe) CO, Na (Wishcenus, A 125, 49)—Potassium salt crystallises with difficulty—BaA', 4aq (at 100°): large cauliflower-like bun lles of rectangular needles (Hans Meyer, B 19, 2454) Deliquescent, v sol dilute alcohol, insol absolute alcohol and ether — BaH₂A'₄ crystals, v sol water Not altered by exposure to air —CaA'₂5aq small white mammillated crystals (from water or alcohol) S 105 in the cold Extremely soluble in boiling water Sol hot, nearly insol cold, alcohol At 100° it becomes CaA', and at 280° it is converted into CaC_aH_aO_a (Wurtz a Friedel, A Ch [8] 63, 184)—CaH_aA', 3aq crystals resembling wavellite, sol absolute alcohol (Engel-hardt a Maddrell, A 63, 119) —CaK, A', octa nedra Deposits CaA' when dissolved in war.n water (Strecker, A 91, 352) -CaNa, A', 2aq granules (S) CaClA' aq prisms, v e sol water (E a M) -Ca₂(CHO)(C₂H₂O₂)Cl₂10aq from calcium chloride, formate, and lactate (Böttinger, A 188, 329) Long needles—SrA', 3.q very soluble—MgA', 3aq prisms, insol alcohol, less soluble than the corresponding sarcolactate S 36 in the cold, 167 at 100° -Al, A', triclinic octahedra (Hans Meyer, B 19, 2454)—AlNa, A', 5aq rectangular prisms and tables—FeA', 3aq small greenish crystals S 2 1 at 10°, 8 5 at 100° Insol alcohol—Ferric lactate is a brown amorphous deliquescent mass, v sol water -MnA', 3aq amethyst coloured monoclinic crystals, m sol cold, v sol hot, water — CoA'23aq peach blossom coloured needles, nearly insol cold, m sol boiling water, insol alcohol -NiA'23aq apple green needles - ZnA', 3aq shining crusts, or large crystals irregularly grouped S 107 at 8° (Buff A 140, 160), 18 at 10° (Wishcenus, A 126, 228), 19 at 15° (Strecker A 105, 316), 167 at 100° Almost insol alcohol, which partly con Almost insol alcohol, which partly con verts it into amorphous ZnA', aq, which again takes up 2aq when exposed to the air (Klimenko, J R 12, 98) —ZnA N,H_e—ZnA',N,H_e (Lut schak, B 5, 30) —ZnNa,A', 2aq —CdA', small needles Anhydrous when deposited from a boiling solution Insol alcohol S 10 in the cold, 12 5 at 100° —BiC₆H₁O₆ (Brüning, A 104, 194) — CuA'₂ 2aq dark blue monoclinic tables (Schabus J 1854, 40a) S 167 in the cold, 45 at 100° S (alcohol) 9 in the cold, 4 at Decomposed at 200° giving aldehyde, lactide, and CO₂ (Engelhardt, A 70, 249) — CuC,H₄O₃ v sl sol water —Hg₂A'₂ aq rosecoloured or crimson crystals, sl sol water, ob tained by mixing the boiling solutions of mercurous nitrate and sodium lactate (E a M)-Prisms of the mercurous salt Hg,A', are also formed by boiling aqueous lactic acid with HgO (Bruning) —SnC₂H₄O₂ crystalline powder, insol water — PbA'₂ gummy, v sol water —PbC₂H₄O₃ (Moldenhauer, A 131, 333) —Pb₂A'₂O₂ aq heavy granular pp, formed when lactic acid is mixed with lead acetate and alcoholic NH_a—UrOA' yellow crystal line crusts — AgA' aq silky needles S 5 in the cold V sol hot, nearly insol cold, alcohol

Nitroxyl derivative
CH₂ CH(ONO₂) CO₂H SG 135 Formed
by dissolving lactic acid in a mixture of cone
HNO₂ and H₃SO₄, and ppg with water (Henry,
B 3, 532) Thick oil Sl sol water v e sol
ether Decomposes in the cold into HCy and
example acid (Henry, B 12, 1837)

Acetyl derivative C, H,O, 1.e CH, CH(OAc) CO,H [167°] (Siegfried) Formed by heating ethyl lactate with Acol and saponifying the product by heating it with water at 150° for 3 hours (Perkin, Z 1861, 166, Wislicenus, A 125, 60) Formed also by boiling a solution of zinc acetate and sarcolactate or lactate (Siegfried, B 22, 2715) Occurs in extract of meat. Thin needles, v e sol water Inactive tile with steam Decomposed by long boiling with water into acetic and lactic acids Bases quickly effect this decomposition When first prepared it is soluble in alcohol, but on keeping it becomes insoluble in alcohol, does not then melt below 300°, and is saponified with great difficulty by alkalis HI produces no \$ 10dopropionic acid — BaA'24aq brittle gumlike mass, v sol water, sol alcohol —Copper salt amorphous deliquescent bluish green mass— ZnA'₂ gummy mass Its solutions become quickly acid, from conversion into acetic acid and zinc lactate

Benzoyl derivative C₁₀H₁₀O₄ te CH₂CH(OBz) CO₂H [112°] S 25 in the cold Obtained by heating lactic acid with benzoic acid at 180° (Strecker, A 80, 42, 91, 360) Formed also by the action of BzCl on calcium lactate (Wislicenus, A 183, 277) Tables or needles, m sol boiling water, v sol alcohol and ether Converted by boiling water into benzoic and lactic acids When recrystallised from water benzoyl lactic acid is always accompanied by an oily hydrate C₁₀H₁₀O₄ aq, which in dry air is slowly converted into the crystalline acids—BaA', 6aq thin six sided plates—AgA'

acids—BaA', 6aq thin six sided plates—AgA'
Amide C,H NO, ie CH, CH(OH) CONH,
[74°] Obtained by the action of gaseous or
alcoholic NH, on lactide (Wurtz a Friedel, A Ch
[3] 63, 108) Formed also by saturating ethyl
lactate with ammonia and allowing the liquid to
stand (Bruning, A 104, 197), and by heating
ammonium lactate in a slow current of dry NH,
at 130° (Engel, C R 98, 574) Small prisms, v
sol water and alcohol Does not combine with
acids or bases, but is decomposed by them on
boiling into NH, and lactic acid

Benzoyl derivative of the amide CH, CH(OB2) CONH, [124°] From benzoyl lactic ether and alcoholic NH, (Wislicenus, A 133, 257) White needles, may be sublimed, sl sol water, v sol alcohol Resolved by boiling KOH into lactic and benzoic acids and NH, Prolonged treatment with alcoholic NH, forms benzamide and lactamide

Isomeride of the amide C₄H,NO₂ Formed by heating ammonium lactate in a cur rent of dry NH₂ at 100° (Engel, C R 98, 574) Pale amber coloured syrup Decomposes at 200° In contact with water it immediately forms ammonium lactate

Ethylamide CH, CH(OH) CO NHEt [48°] (260°) From lactide and NH,Et Crystalline (Wurtz a Friedel, A Ch [3] 63, 110) Decomposed by alkalis into ethylamine and lactic acid

Antitée C. H. 1NO; te CH. CH (OH) CO NHPh [58°] Formed by heating lactic ether with aniline *t 150° (Leipen, M 9, 48) Colourless prisms, sl sol water, insol ligroin, v sol ether, chloroform, and alcohol. o-Tolusde C₁₀H₁₃NO₂. [72°] From o-toluidine and lactic ether Crystalline powder [72°] (from benzene) Insol ligroin (Laipen, M. 9, 50, 51)

p.Tolusds C, H, NO, ss CH, OH(OH) CO NHC, H, Me [102°] From toluidne and ethyl-lactate White needles [102°] From p-

sl sol water

Cyanamide CN NH(CO CH(OH) CH₃) Formed by dissolving lac-Lacto-cyanamide tide (20 g) in a strong alcoholic solution of potassic cyanide (16 g), passing in CO₂ to remove free alkalı and evaporating to crystallisation (Mertens, J pr 125, 33) It forms a silver

Methyl ether C,H,O, 16 CH, CH(OH) CO Me (145° 1 V) S G § 1 1180 (Schreiner, A 197, 1, B 12, 179) Colourless neutral liquid Combines with CaCl2. Is imme-

diately decomposed by water

Ethyl ether C₃H₁₀O₃ * e

CH₂CH(OH) CO₂Et

Ethyl lactate (154 5°

1 V) S G § 1 0546 Formed by distilling cal (154 5° cium lactate with KEtSO, (Strecker, A 81, 247 91, 355) Formed also by heating lactic acid (dried at 145°) with alcohol (F a W) and by passing alcohol vapour into lactic acid at 175° (Wishcenus, A 125, 58) Colourless liquid, immediately decomposed by water (Schreiner) Forms with CaCl, the compound CaCl, 4EtA Colourless liquid, crystallising in granules Chloral gives a liquid compound, whence phosphorus pentachloride forms liquid CCl₃ CHCl O CHMe CO₂Et S G ¹¹ 1 42 (Henry, Bull Acad Roy Belg [2] 37, No 5) Lactic ether is a weak hypnotic (Pellacani a Bertoni, C C 1887, 1149)

Acetyl derivative of the ethyl ether CH, CH(OAc) CO₂Et (177°) at 733 mm V D 5 70 (calc 554) SG 17 1046 From ethyl lactate and AcCl (Wishcenus, A 125, 58) Neu tral oil, gradually decomposed by water into alcohol and CH₂ CH(OAc) CO₂H Miscible with

alcohol and ether

Bensoyl derivative of the ethyl ether CH, CH(OBz) CO₂Et (288° cor) From ethyl lactate and BzCl at 100°, or from silver benzoyllactate and EtI (Wislicenus, A 133, 272) miscible with alcohol and ether Resolved by water at 150° into lactic acid and benzoic ether Alcoholic NH, gives CH, CH(OBz) CONH,

Nitroxylderivative of the ethylether CH₄ CH(ONO₂) CO₂Et (178°) S G 13 1 153 From ethyl lactate, HNO, and H2SO, (Henry,

B 3, 532)

Butyryl derivative of the ethyl ether CH, OH(O C4H,O) CO2Et (208°) SG 2 1 024 From a chloro-propionic ether and potassium butyrate (Wurtz, A 112, 235)

Isopropyl ether CH, CH(OH) CO.Pr

(167°) (Sılva, Bl [2] 17, 97)

Ethylidene ether CH, CH CO O Formed by heating lactic acid with

acetic aldehyde at 150° (Leipen, M 9, 46). Liquid, al sol water Quickly decomposed by hot water into its components

Tri-chloro-ethylidene ether

CH, CH<O O CH COI. [45°] (228°)Prepared by heating syrupy lactic acid with excess of chloral for a short time at 150°, and

distill ng the product with steam (Wallach, A. 193, 1) Colourless crystals, readily sol alcohol,

ether, and CS₂, insol water

Methyl derivative C₄H₂O₂ is

CH₄ CH(OMe) CO₂H

The Na salt is formed, together with the methyl ether, by treating CH, CH(ONa)CO,Na with MeI The free acid is a syrup, volatile with steam. It forms an amorphous silver salt O4H,AgO3, v sol water

Methyl ether of the methyl derivative C₁H₁₀O₃ ve CH₃ CH(OMe) CO₂Me (135°-138°) (Markownikoff a Krestownikoff, A 208, 343) From basic sodium lactate CH₃ CH(ONa) CO₄Na and MeI (Wislicenus, A 125, 53)

Ethylether of the methyl derivative C_eH₁₂O₃ re CH₂ OH(OMe) CO₂E (135 5° 1 V). SG § 9906 From a bromo propionic ether and NaOMe (Schreiner, A 197,1) Colourless liquid, nearly insol water

Ethyl derivative C, H,O, 1e

CH, CH(OEt) CO2H Ethyl lactre acid (195°-198°) Obtained by decomposing its ether CH, CH(OEt) CO.Et with caustic potash or lime Formed also, together with CH.I. and acrylic acid, by the action of NaOEt on iodoform (Butlerow, A 114, 206, 118, 325, BL 1861, 9) Liquid, partly decomposed by distillation Miscible with water, alcohol, and ether, but separated from its aqueous solution by CaCl, or Na₂SO₄ Decomposes carbonates Alkalis do not convert it into lactic acid and alcohol When heated with conc HIAq there is formed lactic acid and EtI

Salts - CaA', 2aq flat prisms, v sol water -AgA' bunches of slender silky needles (from hot water)

Ethyl ether of the ethyl derivative C,H,O, ie CH, CH(OEt) CO,Et (155° 1 V) (Schreiner, B 12, 179) SG 8 9498 VD 505 (calc 506) Formed by the action of NaOEt on a chloro propionic ether (Wurtz, A Ch [3] 59, 169) Formed also by treating lactic ether with sodium and EtI (Wurtz a Friedel, A Ch [3] 63, 103) Also from silver ethyl lactate and EtI Colourless liquid, nearly insol water, sol alchohol and ether convert it into alcohol and ethyl lactic acid

Amide of the ethyl derivative CH, CH(OEt) CONH, Lactamethane [68°] (219°) Formed by allowing CH, CH(OEt) CO,Et to stand a few days with aqueous NH, (Wurtz, A Ch [3] 59, 174) Broad plates, sol water, alcohol, and ether Decomposed by distillation

with potash into NH, and lactic acid

Phenyl derivative CH₂CH(OPh) CO₂H.
Phenoxy propionic acid [113°] Formed from
a chloro propionic acid (25 g), strong caustic
soda (to neutralisation), and sodic phenylate
(24 g) The liquid is evaporated till it becomes (24 g) thick, dissolved in water, and treated with HCl (L Saarbach, J pr 129, 152) Glassy needles (from water) Sl sol cold water, volatile with steam, v sol hot water, alcohol, and ether. Aqueous solutions give a yellow pp with FeCl, Its salts are soluble in water —NaA' Exhibite rotatory action while dissolving in water Deliquescent —KA'1 aq at 180° — CaA', 2aq —AgA'; sharp needles, blackened by light

Ethyl ether of the phenyl derivative Eth. (244°) SG 1860 Formed when an alcoholic solution of the acid is allowed to standMore rapidly by passing HCl into such a solu-

Amide of the phenyl derivative CH, CH(OPh) CONH, [130°] Formed from the ether by aqueous ammonia Crystallises V sol alcohol from hot water in long needles and ether Dissolves in hot HCl, on cooling crystals of the hydrochloride of the amide separate

Bromo-pheryl derivative

OH, CH(OC,H,Br) CO₂H Bromo phenoxy pro-prome acid [106°] Formed by the action of bromine water on a solu ion of phenylated lactio acid Crystallised from alcohol V sol. alcohol and ether, sl so water Boiling aqueous NaOH cannot turn out the bromine, 'tence Br is in the benzene nucleus (Saarbach, J pr [2] 21, 157) — NaA' Deliquescent needles

Thymyl derivative CaH.PrMe O CHMe CO2H Formed by heating thymol with a chloro propionic soid in presence of a 50 pc solution of KOH, acidifying with HCl, and adding ammonium carbonate (Scichi lone, G 12, 48) The acid from synthetical thymol crystallises in prisms [74°], v sol alco hol, ether, and chloroform The acid from natural thymol crystallises in needles [48°], and forms very soluble and amorphous Ba and Ag

p Benzyl-phenyl derivative C.H. CH.C.H. O CHMe CO.H [102°] From p benzyl phenol, KOH, and a-chloro propionic acid (Mazzara, G 12, 264)

Benzyl p-tolyl derivative C₄H, CH, C₄H, Me O CHMe CO₂H [1150] Small crys-Formed in like manner (Mazzara) tals, sl sol water, v sol alcohol and ether solutions give a yellow turbidity with ferric salts and crystalline pps with lead acetate and AgNO,

Allophanyl derivative

NH, CO NH CO O CHMe CO, H [190°] Formed by passing gaseous cyanic acid into an ethereal solution of lacticether and saponifying the result ing allophanyl lactic ether with conc HClAq at 100° (Traube, B 22, 1572) Minute colourless needles, m sol cold, v e sol boiling, alcohol or water When heated above 190° it splits up into lactic and cyanic acids -AgA' white powder, decomposed by boiling water -PbA',

orystalline pp

Ethyl ether of the allophanyl derivative Et!' [170°] Colourless needles, v sol hot alcohol and hot water, v sl sol ether Decomposed by alkalis into CO2, ammonia, alcohol, and lactic acid Ammonia yields

biuret

Isoamyl ether C,H,A' [131°]. Monobasic anhydride

C_cH₁₀O₃ ie CH₃ CH(OH) CO O CHMe CO₂H Dilactic acid Formed when aqueous lactic acid is left for several months over sulphuric acid in vacuo (Wislicenus, A 164, 181) quires 1 mol of KOH for each mol of C.H,O, to neutralise it, but the neutral solution gradu-

ally becomes acid from liberation of free lactic acid, potassium lactate being also formed By heating lactic acid at 140° this anhydride is formed together with lactide It may also be

Vor III

amorphous Mg and Casalts The ethyl ether CH, CH(OH) CO O CHMe CO2Et (c 235°) 8 G 2 1 134 is formed by the action of chloro-proplonic ether on potassium lactate (Wurtz a Friedel, A Ch [3] 63, 112) It is decomposed when heated with water into lactic acid and alcohol

Distributed by the Distributed by the Distributed C₁₀H₁₈O₃ are (CH₂CH(CO₂Et))₂O or CH₃CH(OEt) CO O CHMe CO₂Et (190° and CH₃CH(OEt)) CO O CHMe CO₂Et (190° and CH₃CH(OEt)) CO O CHMe CO₂Et (190° and CH₃CH(OEt)) vacuo) Formed by treating a-chloro propionio ether with CH₁ CH(ONa) CO₂Et at 115° (Britg gen, A 148, 224) Scarcely attacked by conc Scarcely attacked by conc KOHAq Alcoholic KOH gives lactic acid and ethyl lactic acid NH, in ether forms an oily amide C₈H₁₅NO₄, decomposed by KOH giving lactic and ethyl-lactic acids

Neutral anhydride C.H.O. s.c.

сн, сн<0 со осн сн, Lactide [124 59] (255°) V D 481 (calc 496) (Henry, B 7, 753) Formed by the dry distillation of lactic acid (Gay Lussac a Pelouze, A 7, 43, Pelouze, A 53, 116, Engelhardt, A 70, 243, Wurtz a Friedel, A Ch [3] 63, 101) Prepared by pass ing dry air through lactic acid at 150° (Wish cenus, A 167, 318) Monoclinic tables (from alcohol) May be sublimed V sl sol. hot water, but gradually converted thereby into lactic acid Bases quickly convert it into lactic acid Ammonia gives lactamide Ethylamine gives the ethylamide of lactic acid CH, CH(OEt) CO,Et forms a compound C₁₂H₂₂O, (270°) decomposed by potash into alcohol and lactic acid

Nitrile C.H.NO is CH, CH(OH) CN Aldehyde cyanhydrin (183°) Formed in the cold by allowing a mixture of aldehyde (1 mol.) and anhydrous HCy to stand for 9 days (Max well Simpson a Gautier, Bl [2] 8, 277) Liquid, not solidified at -21° Partially decomposed into its components by distillation Miscible with water, alcohol, and ether Aqueous KOH forms KCy and aldehyde (or aldehyde resin) Conc HClAq acts violently upon it, at 0° the products are lactic acid and NH,Cl

Sarcolactic acid C3H6O, 1 e

CH, CH(OH) CO H Paralactic acid (Heintz, P 75, 391) [a]_D = 35° Occurs in muscular tissue, thymus and thyroid gland, urine after much exercise, spleen, lymphatic glands, and in pig's bile (Liebig, A 62, 278, 326, Wishcenus, A 167, 302, Strecker, A 123, 354, Colasanti a. Moscatelli, H 12, 416, G 17, 548, 18, 548, Marceuse, B C 1887, 92, Nebelthau, Zent Brol 25, 123, Hirschler, H 11, 41, Gleiss, Pf 41, Sarcolactic acid is absent from living blood, but occurs in blood after death (Salomon, Virchow's Archw, 113, 356, of Berlinerblan, C C 1888, 757, Vissokovitch, C C 1888, 117) Sarcolactic acid may occur sometimes along with ordinary lactic acid as a product of fermentation (Maly, B 7, 1567) Its presence is then due to micrococcus acidi paralactici, which can convert glucose into sarcolactic acid (Nencki a Sieber, M 10, 532) Sardolactic acid is formed in the fermentation of inosite by cheese (Helger, A 160, 336) It is also formed by the action of nitrous acid on the formed from a-bromo propionic soid and potas-sum lactate (Brüggen, Z 1869, 388) It forms amido propionamide present in urine A dextrorotatory lactic acid is formed by the action of Pemcelleum glaucum on ordinary ammonium

lactate (Lewkovitch, B 16, 2720)

Preparation.—1 Chopped fiesh is exhausted with cold water, the extract mixed with baryta water, the albumen coagulated by boiling and removed by filtration, and the clear liquid concentrated by evaporation Sulphuric acid is added to the syrupy residue, and it is shaken with ether, which leaves sarcolactic acid when evaporated —2 Extract of meat (1 pt) is dissolved in warm water (4 pts) and ppd with 90 p.c. alcohol The filtrate is evaporated to a syrup, mixed with 4 pts of alcohol, filtered, evaporated, acidified by H₂SO₄ and extracted with ether (Klimenko, J. R. 12, 17, Bl [2] 84, 321)

Properties — Dextrorotatory syrup, forming levorotatory salts Resembles ordinary lactic acid in its reactions. In a dry atmosphere it changes in the cold to a levorotatory anhydride $[a]_D = c - 86^\circ$ At 140° it forms ordinary lactide, whence water produces ordinary inactive

lactic acid (Strecker, A 105, 313)

Reactions—1 Hot dilute sulphuric acid

splits it up into formic acid and aldehyde—2

Chromic acid maxture gives CO, and acetic

acıd

Salts —CaA'₂4aq (Engelhardt, A 65, 359) S 8 in the cold V sol boiling water and alcohol —CaA'₂5aq changes into CaA'₂5aq on recrystallisation —MgA'₂4aq More soluble in water and alcohol than ordinary magnesium lactate —NiA'₂3aq —ZnA'₂2aq Forms more distinct crystals than ordinary zinc lactate S (of ZnA'₂2aq) 57 at 145°, the solubility of ordinary zinc lactate being 17 (Wislicenus) S (98 pc alcohol) 104 —ZnA'₂3aq Ppd by adding alcohol to an aqueous solution of the zinc salt —AgA'₂aq flat needles

zinc salt —AgA' $\frac{1}{2}$ aq flat needles Ethyl ether EtA' [a]_D = -14 2° From the silver salt and EtI (Klimenko)

Chloro lactic acid v Chloro oxy-propionic

Chloride of lactic acid v Chloride of a-Chloro-propionic acid

LACTIDE v Neutral anhydride of Lactic

LACTIM A compound of the form C OH (Baeyer, B 15, 2093).

LACTIMIDE C.H.NO 1.6

CH_s CH CO_{NH} [275°] Produced together with ethylamine and CO₂ by heating alanine in dry HCl at 190° as long as water comes off (Preu, A 134, 872) The brown amorphous product is treated with lead hydroxide and H₂S and recrystallised from alcohol Colourless needles, may be sublimed V sol water and alcohol Has a bitter taste Its solution does not dissolve Ag₂O or give a pp with ZnCl₂ or AgNO₃

LACTO-ALBUMEN v Milk LACTO-ALBUMOSE v Milk

LACTO-EIONIC ACID $C_{12}H_2O_{12}$. Formed by treating a solution of milk sugar (1 pt) in water (7 pts) with bromine (1 pt) at ordinary temperatures for some days, the bromine is next removed by a stream of air and H_2S , the HBr is

removed with white lead followed by Ag₂O and the metals with H₂S, on treating the syrup so obtained with glacial acetic acid the lacto bionic acid is left. The product is purified by conversion into lead salt, with specially prepared basic lead acetate, and decomposition of the same with H₂S (Emil Fischer a Jacob Meyer, B 22, 362) Colourless syrup of strong acid reaction, v sol water, v sl sol alcohol, insol ether. Shows no tendency to crystallise. Does not reduce alkaline copper solutions even on boiling. On warming a short time with dilute mineral acids it splits up into galactose and gli come acid.

C₁H₂O₁₂ + H₂O = C₈H₁O₄ + C₆H₁O₇

LACTOCYANAMIDE v Lactic actic, p 112

LACTONES Anhydrides of oxy acids formed by elimination of water between the hydroxyl and carboxyl groups, both being in the same carbon chain The name is derived from lactide which, until its vapour density had been determined, was written CH₃ CH $\stackrel{\circ}{CO}$ Lactones are usually derived from γ - or from δ oxyacids The formula $R''R'C \stackrel{\circ}{CH_2} CH_2$ represents a γ lactone, while

R''R'C < CH₂·CH₂ > CH₂ is a 8 lactone (Fittig, A. 200, 21, 208, 67, 216, 52)

200, 21, 209, 67, 216, 52)

Formation—1 γ Oxy acids split up in the cold, and immediately on heating their aqueous solution into water and a γ-lactone—2 Formed by boiling their carboxylic acids with dilute H.SO₄ (Erdmann, A 228, 176)—3 From ethers of γ oxy acids on distillation, alcohol being split off, eg oxy iso caproic ether (Bredt), oxy valeric ether (Kissling)—4 From unsaturated acids (v A 227, 8, 26), eg

Properties —Volatile liquids, neutral to litnus Volatile with steam

Reactions -1 7 Lactones do not take up water to form an oxy acid by mere boiling the other hand most 8 lactones in presence of water, cold or hot, are partially converted into acid, and tend to assume equilibrium with 65 pc of lactone to 35 pc of acid (Fittig a Wolff, A 216, 187, Hantzsch, A 222, 28) — 2 All lactones are converted into salts of the corresponding oxy acids by boiling with aqueous solutions of alkalis, alkaline earths, and sometimes even with CaCO, (Fittig, A 208, 116). 3 All lactones form compounds with NH3, which easily split up into their components (Wolff, A 229, 278) These compounds are pro-bably acid amides—4 No lactone at present known reacts with hydroxylamine, but a few aromatic lactones readily react with phenyl-hydrazine (e.g. phthalide) Hence the fact of an oxygen compound reacting with phenyl hydrazme cannot be taken (as previously assumed) as a proof of its aldehydic or ketonic nature This can only be proved by its behaviour towards hydroxylamine (V Meyer a Münchmeyer, B 19, 1706) The compound formed with phthalide appears to be HO CH, C,H, CO N,H,Ph being formed by direct addition (Wisheams, B 20, 401)—5 Lactones (1 mol) appear to react with oxalic ether (1 mol.) in presence of NaOEt (1 mol) Phthalide gives C₁₂H₁₀O₃ [122°] and | valerolactone also gives a crystalline compound (Wishcenus, B 20, 2061)

Lactones are for the most part described in this Dictionary under the oxy acids of which

they are the anhydrides LACTONIC ACID v GALACTONIC ACID

Lactonic acids Acids which are at the same time lactones When warmed with alkalis they give rise by assimilation of water to acids of higher basicity

LACTONITRILE v Nitrile of Lactic acid

LACTO-PROTEIN v MILE

LACTOSE or Milk sugar v Sugar and Milk LACTOSIN O36H62O31 Occurs in the roots of all the caryophyllacese, being most conve niently obtained from Silene vulgaris (A. Meyer, B 17, 685) White amorphous powder (anhydr), $[a]_D = +168$, or small glistening crystals $(+H_2O), [a]_D = +2117$ It forms gummy solu tions with water, but is sparingly soluble in alcohol The aqueous solution of the crystal lised lactosin gives no pps with neutral or basic lead acetate, although a pp is produced by lead acetate and NH. Fehling's solution is not re duced on short boiling By boiling with dilute H₂SO₄ it is inverted into lactose and a new sugar

LACTUCARIUM A brownish "isoid sub stance obtained by evaporating juice which exudes from incisions in the leaves and stem of certain species of lettuce, especially Lactuca vwosa It has an odour resembling opium and acts as a narcotic According to Ludwig (Ar Ph [2] 7, 129) it contains (50 p c of) 'lactucone' C₁₀H₈₆O₂, a crystalline substance [150°-160°] soluble in boiling alcohol, 'lactucic acid,' lactucin, a wax, and oxalic acid According to Hesse (A 234, 243) lactucarium contains the acetyl

derivatives of (a) and (B) lactucerol

LACTUCERIN C₄₀H_{el}O₃ (L), or C₂₂H_{el}O₂ (K),
or C₁₂H_{e2}O₃ (H) Lactucone [210°] Obtained
by washing lactucarium with benzene and extracting the residue with boiling alcohol, the crystals obtained may be purified by shaking their ethereal solution with aqueous KOH, and ppg by the addition of alcohol and water (Lenoir, A 60, 83, Kassner, A 238, 220) Lactucerin so prepared forms minute white needles [200°], but after sublimation in CO₂ it melts at 210° On fusion with KOH it gives lactucel On fusion with KOH it gives lactucol C, H20, hydrogen, and acetic acid It is dextrorotatory According to Hesse, lactucerin consists of the mono-acetyl derivatives of (a) and (B) lactucerol From the milk juice of lactuca canadensis, by crystallising from hot alcohol Flowers (Ph [3] 10, 44) obtained a 'lactucern' [89°] crystallising in colourless needles

Lactucone C, H₂₄O(?) [296°] Microscopic Insoluble in water, difficultly soluble needles in alcohol Occurs in French lactucarium from Lactuca altissima, from which it is extracted with 90 pc alcohol Acetic anhydride does not act upon it even at 200° By distillation with P.S. it gave a hydrocarbon of the constitution $C_{14}H_{22}$, boiling between 247°-252° (Franchimont, B 12, 10)

Lactucol C, H, O [1629] Obtained by fusing lactucern with KOH (Kassner, A 238, 224) Needles Dextrorotatory, [a]₀ = 46° Acetyl derivative C₁₈H₁₈AcO [200°]

Like lactucel and lactucerin its solutions in ether, chloroform, and CS, are dextrorotatory, $[\alpha]_D = 68^\circ$

(a)-LACTUCEROL C, H 60 O, [166°-181°]. Obtained by exhausting lactucarium with ligroin and extracting the residue with alcohol crystals so obtained are saponified by alcoholic potash, and the product ppd with water pp is recrystallised from alcohol, from which (a) lactucerol separates first (Hesse, A 234, 245,

244, 268)

Properties — Crystallises from 90 p c alcohol in silky needles (containing 2aq) From chloroform or ether it separates in anhydrous crystals. Insol water and alkalıs It melts at 162°, but after purification by conversion into its di-acetyl derivative and saponification of the product its melting point is higher Conc H₂SO₄ colours its solution in chloroform red It absorbs Br with It is dextrorotatory, in a 2 3 evolution of HBr p c solution in chloroform $[a]_D = 76.2$ at 15° It may be distilled in a current of CO2

Acetyl derivative C36H59AcO [202°-207°] Occurs in lactucarium, and is formed by heating (a) lactucerol for a short time with Ac.O at 80° Small plates, m sol cold alcohol, v sol

ether Dextrorotatory

Di-acetyl derivative C,6H,58Ac2O [1980-200°] From (a) lactucerol and Ac2O by boiling for 2 hours Satiny plates In a 1 pc solution in chloroform $[\alpha]_D = 63.6$ at 15°

D: propionyl derivative
C₁₄H₁₅(C₅H₅O),O₂ [152] Minute needles (from alcohol), v e sol CHCl₂ and ether

Di-bensoyl derivative CacH,sBz2O2 [156°] White crystals, insol water, v sol ether and chloroform, sl sol alcohol Saponified by alcoholic potash

(β)-Lactucerol $C_{10}H_{50}O_2$ [α]_D = 38 at 15° in a 4 p c solution in chloroform Occurs as a mono acetyl derivative in lactucarium, and separated from its (a)-isomeride by crystallisation from alcohol Long silvery needles (from ether or chloroform) Separates from alcohol as a gelatinous mass (containing 2aq) More soluble in alcohol, and less dextrorotatory than its iso meride

[230°] Acetyl derivative C36H39Ac2O Plates (from alcohol) Less sol alcohol and

ligroin han its isomeride

LACTUCIC ACID Obtained from the juice of Lactuca canadensis after separating 'lactucerin,' adding water, ppg with lead acetate, decomposing the lead salt with H₂S and evaporating (Flowers, Ph [3] 10, 44) Brownish green amorphous substance, with acrid, bitter taste. Sol alcohol, insol petroleum spirit, ether, and chloroform Ludwig (J 1847, 824) and Walz (N Jahr Pharm 15, 118) obtained a substance (C40H38O19?) called lactucic acid by triturating lactucarium (1 pt) with dilute H₂SO, (1 pt), adding alcohol (5 pts of 84 pc), filtering, shaking the filtrate with slaked lime, decolourising with animal charcoal, evaporating, and crystallising the residue from boiling water yellow amorphous mass, gradually becoming crystalline Its solutions are colouled wine-red by alkalis, and reduce boiling Fehling's solution.

LACTUCIN C., H., O15 or C., H., O, or C., H., O5.
S 1 25 in the cold Occurs in the juice of common lettuce (Lactuca sativa) and of Lactuca

LACTUCIN 116

altissima (Aubergier, B J 24, 522, A 44, 299, Walz, A. 32, 85, N Jahr Pharn 15, 118, Ludwig a Kromayer, Ar Ph [2] 111, 1, Kromayer, Ar Ph [2] 105, 3, Buchner, Rep Pharm 43, 1, Flowers, Ph [3] 10, 44) Obtained by macerating the dried juice with hot water (1) pt) for four days, pressing the mass, boiling the residue with water, and ppg the filtrate with lead subacetate, removing excess of lead from the filtrate by H2S, and evaporating Pearly M sol alcohol and scales (from alcohol). HOAc, sl sol ether Conc HNO, turns it brown Its solutions are not ppd by ordinary reagents

LACTUCOPICRIN C44H84O21. An amorphous very bitter substance which remains in the mother-liquor in the preparation of lactucin (Kromayer, Die Bitterstoffe, 1861, Flowers, Ph [3] 10, 222) Sol water and alcohol, its solutions not being ppd by lead salts

LACTURAMIC ACID v URAMIDO PROPIONIO

LACTYL CHLORIDE is the chloride of

a-Chloro propionic acid CS NH CH CH. LACTYL-THIO-UREA NH CO

From this urea and a chloro propionic ether at 100° (Freytag, J pr [2] 20, 380) LACTYL-UREA C4H4N O2 1 c. Crystalline.

NH CH CH. Methyl hydantoin [140°] NH CO

(H), [145°] (Urech, B 6, 1113) Formed by treating aldehyde ammonia with crude KCy and hydrochloric acid CH₃CH(OH)NH₂ + HCN + HCNO $= NH_2 + C_4H_6N_2O_2$ (Heintz, A 169, 120) Formed also by heating uramido propionic acid Prisms, or cauliflower-like tufts (containing aq), v sol water and alcohol, nearly insol ether May be sublimed Tastes bitter Neutral in reaction May be Boiling baryta water converts it into uramidopropionic acid Heating with barium hydrate at 100°-140° gives alanine Pure HNO, gives a quantitative yield of a nitro derivative, but no gas is evolved (Franchimont, R T C 6, 217) — AgC₄H₂N₂O₃, formed by treating lactyl ures with moist Ag₂O Insol water, sol NH₂Aq Ppd as a white powder by adding HNO, to its ammoniacal solution

LÆVULAN $C_6H_{10}O_5$ [250°] $[\alpha]_D = -221°$ Occurs in an impure condition in the residues obtained from desugarising molasses by Steffen's process (Lippmann, B 14, 1509) White amorphous powder Sol hot water, the solution gelatinises on cooling Bylong boiling it becomes much more soluble and loses its power of gela tinising Insol alcohol It does not reduce Fehling's solution but produces a blue pp By HNO₂ it is oxidised to mucic acid H₂SO₄ at 120° converts it into levulose LEVULIN C₁₂H₂₀O₁₀ (dried at 110°) Dilute

stance resembling dextrin, contained in the juice of the tubers of the Jerusalem artichoke (Hehanthus tuberosus) and of Dahlia variabilie, and ın oak bark (Ville a Joulie, Bl. [2] 7, 262, Popp, A 156, 1814 Dieck a Tollens, A 198, 228, BC 1879, 275, Etti, B 14, 1826, Lefranc, J Ph [5] 2, 216, Reidemeister, J. Th 1881, 68) Frepared by ppg the juice of artichokes with lead acetate, filtering, removing excess of lead by

H.S., neutralising with MgCO, filtering and evaporating The residue is extracted with alcohol, until it is optically mactive It is then extracted with absolute alcohol, which leaves inulin undissolved, and ppd with ether

Properties - Amorphous deliquescent mass, optically mactive, but becomes levorotatory on boiling with dilute HCl, being split up into levulose and glucose V sol water and dilute alcohol, al sol absolute alcohol, insol ether Has an insipid taste Turns brown at 140° forming caramel Not ppd by lead subacetate Peduces Fehling's solution after long boiling Dilute HNO, gives oxalic acid and saccharic Alkalıs do not turn ıt brown acid hydrolysed by yeast and then undergoes alcoholic fermentation Lævulin prevents the ppn of ferric and cupric salts by alkalis AgNO, gives a white pp blackened on heating —K₂C H₁₈O₁₉ ppd by adding alcoholic KOH to its alcoholic solution — Ba₂C₁₂H₁₆O₁₀ aq amorphous - Pb₂C₁₂H₁₆O₁₀ aq amorphous, ppd by adding an alcoholic solution of lead subacetate to an alcoholic solution of lævulin

LEVULINIC ACID v B ACETYL PROPIONIC ACID

LEVULOSE v SUGAR.

LANTHANUM La At w 138 2 Mol w. unknown SG 6163 Melts between MP of Sb (450°) and that of Ag (950°) (Hillebrand a Norton, P 156, 466) S H 04485 (H a N, P 158, 71) S V S 22 4 Chief lines in emission spectrum 5183, 4921, 4920 in the green, 4824, 4655, 4558 in the blue, 4522, 4330, 4268 in the indigo, 4238, 4196, 4086, 4077 in the violet (Thalén) In 1803 Klaproth separated a new earth from a Swedish mineral, the earth was examined by Hisinger and Berzelius and called by them certa (from the planet Ceres then recently discovered) In 1839 Mosander showed that ceria contained two oxides (P 46, the name ceria was retained for one, and the other was given the name lanthana (λανθάνειν = to be concealed) In 1841 Mo sander discovered that lanthana was a mixture of two oxides (v P 60, 297), one of these he called lanthana and the other didymia (δίδυμος = twofold)

Occurrence -As silicate, with silicates of Ce and Di, in cerite, gadolinite, orthite, &c (Ram melsberg, P 107, 631) Lanthante, from Bethlehem in Pennsylvania, US, is a car bonate of La and D1 (Lawrence Smith, Am S [2] 18, 378) La containing mine als occur in small quantities in a few localities

Preparation -The mixed oxides of Ce, La, and Di are separated from cerite by treatment with H2SO4, &c, as described under Cerium (vol 1 p 723), the oxides are dissolved in HNO, Aq, the solution is evaporated to dryness the residue is heated to full redness until pale yellow, and then treated with boiling dilute HNO, Aq in which nitrates of La and Di dissolve while basic Ce nitrate remains insoluble There are various ways of separating La from D₁ in the nitric acid solution. The hydrated oxides may be obtained by ppn with NH₃Aq, the pp is dissolved in H₂SO₄Aq, and the mixed sulphates are obtained by crystallisation, the sulphates are dried and powdered, 1 part is dissolved in small successive portions in 6 parts

water at 2°-8°, the solution is then heated to 6. 40° when La₂(SO₄)₃ separates nearly free from D1₂(SO₄). The La₂(SO₄), may be purified by re solution in ice cold water and heating to 40°, the operations being repeated until the sulphate as perfectly white and shows no Di lines in the spectrum Or the solution of La₂(SO₄), may be ppd by oxalic acid, the pp strongly heated, dissolved in HNO,Aq, and fractionally ppd by NH, Aq, the ppn must be effected from very dilute solutions by means of very dilute NH, Aq, the first third of the pp contains most of the Di oxide, ppn is continued so long as the pp shows Di lines in the spectrum. This method gives good results when comparatively much La 18 present (Mosander, lc, Bunsen a Jegel, P155, 877), but it is slow and laborious Marignac (J pr 48, 406) adds excess of HNO, Aq to the solution of the nitrates of La and Di, heats, and adds oxalic acid, the pp dissolves, when crys tallisation begins the solution is allowed to cool, and is then poured off from the pp which is rich in Di oxalate, these operations are repeated, a very acid solution of La salt is finally obtained from which NH3Aq ppts La2O3xH2O method is recommended when much Di is present with little La.

The method of Von Welsbach (Sitz W 92 [2nd part], 317) was found very go i by Robin son (priv comm) A large quantity of the mixed nitiates of Ce and La obtained from cerite after separating basic Ce nitrate (v vol 1 p 723) is mixed with the necessary quantity of NH₄NO₄, about 10th part cone HNO Aq is added, and the liquid is evaporated until small crystals appear on the surface, a little water is then added, and crystallisation is allowed to proceed for about 24 hours, the crystals are drained and washed with a little HNO, Aq which is added to the mother liquor, the mother liquor is evaporated and crystallised, the liquor from this is again evaporated, and so on until 68 fractions are obtained The first fraction contains almost all the La By fractionating the middle fraction, placing the first fractional pp in the former first fraction, and repeating this process a few times, pure La(NO₃), is obtained For other methods of separating La salts from salts of Ce and Di v Hermann, J pr 82, 385, Erk, Z [2] 7, 100, Cleve, Bl [2] 21, 196, 246

La₂Cl₆ is obtained by dissolving the pp of La₂O₂xH₂O (obtained as described above) in HClAq, adding NH₄Cl, evaporating to dryness, and heating strongly in a covered crucible By reducing La₂Cl₆ by heating with K and washing out KCl in alcohol, metallic La is obtained Hillebrand a Norton obtained approximately pure La by electrolysing La₂Cl₆ covered with a fused mixture of KCl and NaCl, using a thick iron with a sengative electrode and a battery of 4 Bunsen's cells (P 156, 466, of Bunsen, P 155, 633)

Properties and Reactions—White metal, fairly malleable and duotile, rather harder than Ce Oxidises rapidly in dry air, but burns only at temperature considerably higher than that at which Ce burns Decomposes cold water slowly, hot water rapidly Easily dissolved by acids, including cold cone HNO₃, which cearcely acts on Ce

The atomic weight of La has been deter-

mined (1) by converting the oxide into the sulphate and tice versa (Rammelsberg, P 55, 65, Margnac, A Ch [3] 27, 228, [4] 30, 67, Holzmann, J pr 75, 348, Czudnowicz, J pr 80, 33, Hermann, J pr 82, 395, Zschiesche, J pr 104, 174, Erk, Z [2] 7, 106, Cleve, Bl [2] 31, 196, Brauner, C J 41, 75, Crookes, Pr 38, 414, (2) by analysing La iodate (Holzmann, J pr 75, 349), (3) by estimating Cl in La chloride (Hermann, J pr 82, 395), (4) by converting La carbonate into oxide (Hermann, lc), (5) by determining S H of La (Hillebrand a Norton, P 158, 71), (6) by considering the chemical relations of La with other elements in the light of the periodic law

The at w of La was taken for many years as c 922, the oxide was formulated LaO and the chloride LaCl₂ Mendelejeff (v C N 41, 49) proposed to multiply the usually accepted at w by 2, and to regard the oxide as LaO, by doing this he placed La in Group IV along with Ce As the properties of La salts were not much known when Mendelejeff's memoir was published, he did not strongly press the arguments in favour of the position assigned by him to La Fuller investigation showed that the usually accepted at w of La should be increased by one half, that the oxide should be regarded as similar to the oxides of the earth metals (M2O2), and that La should be placed in Group III along with Al, Ga, Sc, &c (v EARTHS, METALS OF THE, vol 11 p 424)

La is distinctly metallic in its chemical relations, it forms the oxide La₂O₃ and there are indications of the existence of a higher oxide, the chloride is La₂Cl₅ or LaCl₃ La forms several

salts of the form LaX₃,
$$X = NO_3$$
, $\frac{SO_4}{2}$, $\frac{PO_4}{3}$

dc, a few double salts and one or two basic salts are known. The investigation of the La compounds shows that this metal is to be placed with the metals of the earths (Group III), it is more closely related to the even series members of the group (Sc, Y, and Yb) than to the odd series members (Al, Ga, In, Tl). The strongly basic character of La, O, marks the connection of La with the alkaline earths and alkali metals. The examination of La compounds is yet far from complete (cf Metals, Rare)

Detection and Estimation—Most of the La salts are colourless, the soluble salts have an astringent, sweetish taste, solutions of La salts do not show any absorption-bands. Alkalis, NH,HS, and KCN, form gelatinous pps insoluble in excess of pptant. Alkali carbonates ppt La.(CO₂)₃, BaCO, forms a pp without warming, H,C₂O₄ forms a white pp at first curdy, then crystalline, more soluble in acids than the oxalates of Ce and Di, Na₂S₂O₃ does not produce any pp. La salts do not colour beads of borax or microcosmic salt.

La may be estimated as La₂O₃ or La₂(SO₄)₃. La O₃ is obtained (1) by ppg with NH₄Aq, washing as rapidly as possible with water containing NH₃ (to prevent formation of La₂CO₂ and partial solution of La), solution in HNO₃Aq, re ppn by NH₃Aq, washing with NH₃Aq, and strongly heating, (2) by ppg La₂(C₃O₄), by addition of H₂C₂O₄ and standing, washing, and heating to white heat La₂(SO₂)₂ is obtained by ppg with

NH.Aq, as above, dissolving in warm dilute H.SO,Aq, evaporating to dryness at 100°, and gradually heating to redness

Lanthanum, arsenate of Lag(HAsO4)3, and arsenite of, La₂(HAsO₂), v Smith, A 191, 331

Lanthanum, borate of (? 2La2O2 B2O3), ob tained, along with crystals of La₂O₂, by dissolving La₂O₃ in molten borax (Nordenskjöld, J pr 85, 481)

Lanthanum, bromide of La, Br, 14H,O, or LaBr. 7H2O. Colourless crystals, e sol water or alcohol, obtained by dissolving La2O, xH2O m HBrAq and evaporating (Cleve, Bl [2] 39, 151, 43, 56) By the action of Br in vapour on La₂O₃, the oxybromide LaOBr is obtained (Frerichs a Smith, A 191, 331) Double salts are described by Cleve (lc) La₂Br₆ 2AuBr, 18H₂O, La₂Br₆ 3ZnI₂ 27H₂O, also by F a S (*lc*), La₂Br₆ 3N₁Br₂, 18H₂O, and La₂Br₆ 3Z₁Br₂, 39H₂O

Lanthanum, carbide of A carbide of La 18 said to be produced by heating the oxalate or formate in absence of air, it is described as similar to, but more easily acted on by acids than, Ce carbide (Delafontaine, C N 11, 253)

Lanthanum, chloride of La,Cl, or LaCl, A

white crystalline mass, e sol water or alcohol Obtained by adding NH₄Cl to a solution of La₂O₃ xH₂O in HClAq, evaporating to dryness, and heating in a closed crucible until all NH₂Cl is volatilised (Hermann, J pr 82, 406, Hille brand a Norton, P 158, 71) Mosander (P M 23, 241) says that LaCl, can be obtained by evaporating La₂O₃ xH₂O in HClAq to dryness,

and heating the residue in a stream of HCl gas By slowly evaporating La₂O₃ xH₂O in HClAq, large colourless triclinic crystals of LaCl, 7H,O are obtained Double salts are described by Smith (A 191, 331), and Cleve (Bl [2] 21, 196, 39, 151) — M 9HgCl, 24H,O, M 2PtCl, 26H,O,

M 8AuCl₂ 21H₂O, M 2AuCl₂ 20H₂O (M = La₂Cl₆) Oxychlorides are obtained by heating the hydrated chloride in air, and by the action of Cl on La2O3 (v Lanthanum, Oxychlorides of)

Lanthanum, chromate of Lag(CrO,), 8H2O,

. Smith, A 191, 355

Lanthanum, cyanide of LaCy, v. vol 11

p. 841

Lanthanum, fluoride of La2F6 H2O A gela tinous pp by adding HFAq to solution of La acetate (Cleve, Bl [2] 39, 151, 43, 56) From solution of La sulphate, Smith obtained a pp of

La₂F₃3HF (A 191, 331) According to Marignao, H₂SiF₅ ppts La₂F₆ from La salts (J pr 48, 406) Lanthanum, hydroxide of La₂O₅H₆, or LaO₄H₅, may also be regarded as hydrated conde La₂O₅3H₅O A white gelatinous pp by adding KOHAq or NaOHAq to solution of a La salt (NH,Aq ppts basic compounds) produced by action of warm water on La2O2 La2O.H. is a strongly basic hydroxide, it turns red litmus blue, decomposes NH, ClAq on warm ing with evolution of NH_2 , absorbs CO_2 from the air, reacts with acids to form salts

$$LaX_s(X = NO_{sp} \frac{SO_s}{2}, \frac{PO_s}{2}, &c)$$
 Thomsen gives

the heat of neutralisation with H280,Aq and HClAq as $[La^2O^4H^4, 3H^4SO^4Aq] = 82,820$; $[La^2O^4H^4, 6HClAq] = 74,970$ (Th. 1, 375).

Lanthanum, haloid compounds of. LaF. LaCl, and LaBr, have been isolated, the formulæ may be written La,F, &c, as none of these compounds has been gasified. All form hydrates, and all combine with haloid compounds of Au and some other heavy metals to form double salts Oxychlorides and oxybromides, LaOX, are known

Lanthanum, 10dide of LaI, has not been isolated, but the double salt 2I al, 3ZnI, 27H,O is described by Frenchs a Smith (A 191, 355)

Lanthanum, oxides of Only one oxide, La2Os, is known with ce 'ainty, there are indi cations of the existence of an oxide containing more O

LANTHANUM SESQUIOXIDE, La2O. by strongly heating La₂O₃ xH₂O, or the oxalate, or any La salt the acid of which is volatilisable Forms a white, amorphous, infusible powder, S G 6 48-6 53 (Cleve, lc, Nilson a Pettersson, B 13, 1464) S H 0749 (N a P, lc, v also Pr 31, 46) Diamagnetic (N a P, lc) Combines with water to form La₂O₃ 3H₂O (v Lanthanum, HYDROXIDE OF) Easily sol in acids Nordenskjöld (J pr 85, 431) obtained La₂O₂ in lustrous rhombic crystals, a b c = 5658 1 6863, S G 5 296, by dissolving the amorphous oxide in borax in a porcelain oven, the crystals did not directly combine with water, but were easily sol in acids The great infusibility of La2O3, and its power of emitting white light when strongly heated, render it useful as a light giver, Von Welsbach has patented an arrangement whereby La₂O₂ is heated in the flame of a Bunsen lamp and emits a clear white light (English Patent, 15,286, July 1886).

LANTHANUM PEROXIDE According to Mosander (P M 23, 241) a peroxide of La is ppd by adding BaO, to a neutral La salt, on drying it loses O Hermann (J pr 82, 397) says that a peroxide is obtained by heating oxalate, nitrate, or carbonate of La in the air, it dissolves in HClAq with evolution of Cl, heated in H it yields La_2O_3 Zschiesche (J pr 104,74) was unable to confirm Hermann's observations Cleve (Bl [2] 43, 56) by ppg La salts by alkalı and H₂O₂Aq obtained an oxide to which he assigned the com position La,O.

Lanthanum, oxybromide of LaOBr Obtained by the action of Br vapour on heated La₂O₂ (Frerichs a Smith, A 191, 331)

Lanthanum, oxychlorides of LaOCl and La₂O₂Cl₂ (=3La₂O₃La₂Cl₂) The former is a greyish mass, unchanged by water, obtained by heating La₂O₂ in Cl to 200° (Frerichs a Smith, A 191, 331, Cleve, Bl [2] 89, 151, 43, 56) The latter is obtained by heating LaCl, 7H₂O and washing the residue with water (Hermann, J pr. 82, 385)

Lanthanum, salts of. La forms one series of salts, LaX, where $X = NO_2$, $\frac{S \cap_4}{2}$, $\frac{PO_4}{3}$, &c Most

of the La salts are colourless, those which are soluble have a sweetish astringent taste. The salts of volatilisable acids yield La₂O₂ when strongly heated La₂8SO₄ combines with the alkalı sulphates, but the products are not alums A good many double La salts are known, a few basic salts have been isolated. The following are the chief La salts . arsenate, arsenute, borate, bromate, carbonate. chlorate, chromate, hypochlorate, vodate, molybdate, nutrate, perchlorate, percodate, phosphates, phosphate, selenate, selenite, silicate, sulphates, sulphates, throsulphate, tungstate, v Carbonates, Nitrates, Sulphates, &c

Lanthanum, sulphide of Ia₂S₃ Red-yellow, microscopic crystals, obtained by the action of 8 parts Na polysulphide with 1 part La₂O₃, and washing with water (Beringer, A 42, 134) Mosander obtained a greyish powder by heating La₂O₃ in CO₂ laden with CS₂ (P 60, 297), and by a similar reaction F with a Smith (A 191, 355) obtained La₂S₃ as a brownish grey powder, soluble in acid—with evolution of H₂S, decomposed by water to LaO₃H₃ and H₂S Didier (C R 100, 1461) obtained a similar body by heating La₂O₃ in H₃S gas M M P M

LAN.HOPINE $C_{73}H_{23}NO_4$ [c 200°] A base homologous with papaverine, occurring in opium (Hesse, A 153, 57, Suppl 8, 271, C C

1870, 168)

Preparation — The aqueous extract of opium is ppd by Na CO₃, the pp dissolved in ether, the ethereal solution shaken with dilute HOAc, and the acid solution poured into aqueous NaOH After 24 hours the ppd thebaïne and papaverine are filtered off, the filtrate neutralised with HCl, ppd by NH₃, and shaken with chlor orm The chloroform takes up codeïne, lanthopine, and meconidine, and is then shaken with dilute HOAc, and the solution exactly neutralised by NaOH, when lanthopine is ppd

Properties — White powder composed of minute prisms (from CHCl₃) Insol water, nearly insol alcohol, v sl sol ether and benzene, m sol chloroform When ppd from solutions by KOH or lime it dissolves in excess of the pre cipitant NH₂ gives a pp insol excess It does not give a blue colour with FeCl₂ Conc HNO₃ gives an orange red colour H₂SO₄ gives no colour in the cold, but a brownish yellow colour at 150°

Salts —The sulphate forms extremely thin needles—B'HCl6aq extremely thin needles, appearing like a jelly when in mass, v sol boil ing water —B'₂H₂PtCl₈2aq lemon yellowcrystal line powder, insol water, alcohol, and HClAq

LANUGINIC ACID C 416 pc, H 73 pc, N 163 pc, S 34 pc, O 314 pc An acid produced by the action of boiling baryta water upon wool (Champion, C R 72, 330, Knecht a Appleyard, B 22, 1120) The excess of baryta is removed by CO₂, the acid ppd by lead acetate, and the pp decomposed by H₂S Yellowish porous mass, v sol hot water, sl sol alcohol, insol ether Its aqueous solution ppts colouring matters as lakes It also ppts tannin and most metallic exides from their acetates It reacts like a proteid with Millon's reagent and with phosphotungstic and

LAPACHIC ACID C₁₅H₁₄O₃ i.e C₁₆H₄O₂(OH)CH CHPr Oxy-amenyl naphtho-

quinone Targuic acid [138°]

Occurrence —A yellow colouring matter present in the 'lapacho' wood of a genus of the Bignoniaces, several species of which are indigenous to the Argentine Republic and other parts of South America (Siewert, Report of Argentine Republic, cap 15, Philadelphia). Oc-

curs also in Greenheart from Surinam (Stein, J pr 99, 3), and in Bethabarra wood (Greene a. Hooker, Am 11, 267)

Preparation—The wood (10 kilos), in the form of saw dust, is boiled with a moderately-concentrated solution of sodium carbonate (500 grms crystallised salt in 80 litres water), the extraction is repeated several times. The solution is of a blood red colour, and the addition of hydrochloric acid precipitates the crude acid together with a red brown resin, from which it is best purified by frequent solution and recrystallisations from benzene (Paternó, G 9, 505, 12, 337, Arnaudon, C R 46, 1152) Yield 5 p.c. of pure material

Properties — Monoclinic prisms, abc = 72061 6492, n = 97 9 (Panebianco, G 10, 80), v sol boiling alcohol, benzene, and ether It dissolves readily in solutions of the alkalis and alkaline earths, forming red solutions containing salts of the acid It decomposes carbonates on boiling

Reactions —1 Completely oxidised by chromic acid —2 Alkaline KMnO₄ gives oxalic acid — 3 Boiling nitric acid (S G 138) yields phthalic acid —4 Distillation with sinc-dust yields isobutylene, naphthalene, and possibly a homologue of naphthalene —5 Boiling with HIAq and phosphorus forms amyl naphthalene (305°) and a little di (B)-naphthyl, both being perhaps derived from an intermediate naphthyl amylene 6 Cold cone HNO₄ (S G 149) or H₂SO₄ gives lapachone —7 Zinc-dust and potash reduce it to an unstable crystalline hydride, re-oxidised by air to lapachic acid

Salts—NaA'5aq scarlet radio-crystalline mass S (of NaA') 15 1 at 24° Sol alcohol—
KA'S 33 3 at 24°—NH₄A'aq large brick red crystals—CaA'₂ aq amorphous red pp S 224 at 24°—BaA'₂ 7aq long slender needles (from boiling water) S 23 at 26°—SrA'₂ aq—PbA'₂ amorphous red pp, insol water—AgA' scarlet powder—Aniline salt C₆H₁NH₂A' [122°], orange prisms (from alcohol)—o-Toluidine salt C₆H₁MeNH₂A' [135°], yellow laminæ—p-Toluidine salt [130°], orange yellow laminæ

Acetyl derivative C₁₈H₁₃AcO₂ [83°]. Formed, together with a compound C₁₉H₁₈O₂ (?), by heating lapachic acid with NaOAc and Ac₂O (Paternò) Sulphur yellow prisms, insol water, sol alcohol, ether, and benzene Readily converted by potash into lapachic acid Br in HOAc converts it into bromo lapachone HNO₂ (S G 148) at 0° forms a nitro-compound C₁₈H₁₂(NO₂)AcO₃[170°], crystallising in reddish plates The compound C₁₉H₁₈O₅ forms small white acicular prisms [132°], v sl sol cold alcohol and ether Boiling alcoholic KOH does not saponify it, but converts it into a compound C₂₆H₂₈O₅, which crystallises (from alcohol) in orange needles [141°] Br does not convert the compound C₁₈H₁₉O₅ into bromo lapachone

Bromo-lapachone C, H, BrO, 26

C₁₀H₄O₂ CHBr O CHPr (?) [140°] Formed by warming lapachic acid with Br in HOAc (Paterno, G 12, 353) Orange lamines, v sol

warming lapachic sold with Br in HOAd (Paterno, G 12, 353) Orange lamine, v sol Lot alcohol, sol HOAc, and benzene, sl sol, ether, insol cold aqueous alkalis. HNOs oxidises it to phthalic acid. Lapachone C, H,O, se

C₁₀H₄O₂<CH₂>CHPr(?) [156°] 'Formed by the action of H2SO, or cold cone HNO, (SG 149) on lapachic acid (Paternò, G 12, 837, Hooker a Greene, B 22, 1723) Silky orange red needles (from alcohol), insol water, v sol hot alcohol and benzene HNO, oxidises it to phthalic acid Distillation over red hot zinc dust gives naphthalene and isobutylene Ac.O has no action Boiling with NaOAc and Ac.O forms a compound C26H26O5, crystallising in brown tables with blue reflex, nearly insol Ac₂O NaHSO₃ forms a white crystalline compound Combines readily with hydroxylamine and with NH, Its molecular weight, found by Raoult's method, agrees with the formula $C_{1a}H_{14}O_3$ Lapachone is converted by heating with alkalis into $C_{10}H_1O_2(OH)$ $CH_2CH(OH)$ Pr, which separates from cold alcohol or HOAc in large crystals [125°], v sol most solvents, readily converted into lapachone by dilute HCl, and forming the salts BaA"aq and Ag,A"aq, both crystallising in red needles

LARCH FUNGUS This fungus extracted with 95 pc alcohol yields a mixture of at least

four different resins (Masing, Ar Ph [3] 6, 111)
(a) C₄₁H₇₇O₈ [125°] S (95 p c alcohol) 3
at 14° Insol chloroform

(β) C₆H₁₀O [90°] S (95 pc alcohol) 7 Sol chloroform

 (γ) $C_{16}H_{30}O_5$ Agaricic acid. [272°] Needles, v sl sol boiling alcohol, insol chloro-

form (Jahns, Ar Ph 221, 269)

(8) A portion easily soluble in alcohol, and partly ppd by water, leaving in solution a resin [C 619 pc, H 81 pc, O 300 pc] S 17, S (alcohol) 17 The resmous mixture is altered by boiling with milk of lime, the pp then thrown down by HCl being separated by chloroform into two substances C_{so}H_{es}O₄, insol chloroform, S (alcohol) 6, and C₃₅H₅₂O₆, sol chloroform, S (alcohol) 2 1

LARDACEIN v PROTEIDS

LARD OIL A nearly colourless fatty oil, obtained by pressing hog's lard SG 20 9122.

un 1 4686 (Long, Am 10, 392)

LARICIC ACID C₁₀H₁₀O₅ [153°] S 1 14at 60° Obtained from the small branches of larch trees (Pinus larix) from 20 to 30 years old (Stenhouse, Pr 11, 405) The bark is exhausted with water at 80°, and the extract evaporated and distilled The distillate is evaporated at 80° and the resulting crystals purified by sublimation monoclinic crystals resembling benzoic acid, usually in twins Sublimes at 93° Volatile with steam Has a bitter astringent taste and powerful odour Reddens litmus slightly sol boiling water and 'alcohol, insol ether tric acid oxidises it to oxalic acid. Its aqueous solution is ppd by baryta water, but not by lead or silver salts Ferric chloride gives a purplered colour The K salt forms flat reddish brown crystals, decomposed by CO2

LARREA RESIN Occurs on branches of Larrea mexicana (Stillmann, B 13, 756) 617 pc of it dissolves in alcohol, 263 in aqueous potash, and 14 p c. consists of a colouring matter

soluble in water

LASERPITIN O₂₄H₂₆O₇ (Feldmann, A 135, 836; Bl. 1866, 1. 457) or O₁₂H₂₆O₄ (Kulz, Ar Ph

[8] 21, 161) [114°] (F); [118°] (K) A bitter principle contained in the root of Laserpitum latifolium Extracted by 80 p c alcohol (F) or by light petroleum (K) Prisms Insol water. sol benzene, chloroform, ether, and CS₂ May be sublimed Its alcoholic solution is ppd by water, but not by alcoholic lead acetate (F) Insol dilute acids and alkalis Conc H.SO. and cone HClAq form deep red solutions (K).
When heated with cone alcoholic KOH it is resolved into angelic acid and laserin C14H22O4 (F) or $C_{20}H_{30}O_{5}$ (K), a crystalline resin, insolcids, sol ether, alcohol chloroform, and HOAc Potash fusion gives methyl crotonic acid and laserin (K)

Laserpitin forms an acetate C15H22O4HOAc crystallising from acetic acid in silky needles (K)

Acetyl derivative C₁₈H₂₁AcO₄ [113°] From laserpiin, Ac₂O, and dry NaOAc (K) Colourless needles, insol water, sol HOAc, alcohol, ether, and CHCl,

Bromo derivative C_{so}H_{so}Br_sO_s [90°] Formed by the action of Br on a solution of laserpitin in CHCl, (K) Needles, sol alcohol, ether, CHCl₃, and HOAc

Di-nitro- derivative C15H20(NO2)2O4 aq [115°] From laserpitin and HNO, (K) Amorphous mass, insol water, sol alcohol, ether, CHCl_s, and HOAc

LAUDANINE C₂₀H₂₅NO₃ (Hesse, A 153, 57, 176, 201, Suppl 8, 272) [165°] S G 1 256 (Schröder, B 13, 1075) S (ether) 155 at 18° $[\alpha]_1 = -135$ in a 2 p c chloroform solution at 22 50

Preparation -An aqueous extract of opium is ppd by lime or Na, CO, the filtrate is shaken with ether, the ethereal solution is shaken with dilute acetic acid, the acetic acid solution is neutralised exactly with NH, the ppd lanthopine is removed by filtration, the filtrate is ppd by excess of ammonia, and the pp crystal lised from ether Laudanine separates first from the ethereal solution, and afterwards codamine. The laudanine is dissolved in acetic acid solution, and the solution mixed with excess of NaOH, which ppts cryptopine The alkaline filtrate is ppd by ammonium chloride, and the pp dissolved in aqueous HOAc, on adding KI laudanine hydro iodide is ppd, and this is de composed by ammonia and the free base crystallised from ammonia

Properties -Stellate groups of small sixsided prisms (from alcohol) Cannot be sublimed Tasteless Lævorotatory In the crystaline state it is v sol benzene, CHCl₃, and boiling alcohol, sl sol cold alcohol, v sl sol ether In the amorphous state it is much more Its salts have a bitter taste their solutions caustic potash and ammonia ppt the base in white amorphous flocks, which soon become crystalline, and dissolve in excess of the precipitant Chloroform extracts the base from the ammoniacal but not from the potash solution Cone H₂SO₄ (containing ferric salt) gives an intense rose red solution, which at 150° changes to dark violet Cone HNO₂ gives an orange-red solution FeCl, gives an emeraldgreen colour The base is poisonous, its hydrochloride acting physiologically like strychnine. Salts —B'₂H₂SO₄4aq concentric groups of

needles, v e sol water, almost insol dilste H₂SO₄—B'HCl 6aq prisms, v sol water and alcohol, v sl sol NaClAq Inactive to light—B'HBr 2aq nodules S 3 5 at 20°—B'HI aq orystalline powder S 2 at 15°, v sol boiling water, insol KIAq—B'₂H₂PtCl₂2aq yellow amorphous pp, v sol boiling water—B'H₂C₂O₄ 6aq concentro groups of delicate needles [110°] S 2 2 % 10°—B'C₄H₄O₄ 8aq [100°] S 4 9 at 15°

LAUDANOSINE $C_{21}H_{22}NO_4$ [89°] S (ether) 5 2 at 16° [a]₁ = 105 in a 2 pc alcoholic solution at 22 5° a = 56 in a 2 pc chlord-

form solution at 22 5°

Preparation - Obtained from opium by ppg the aqueous extract with Na2CO3, dissolving the pp in ether, shaking the ethereal solution with dilute HOAc, and pouring the acid solution into aqueous NaOH The pp contains a large number of bases, and is warmed with alcohol and dilute HOAc, and partially evaporated at 50° Papaverine and narcotine are then ppd, and thebaine and tartrate is ppd by adding tartaric acid to the filtrate. The filtrate is exactly neutralised with NH3, and NaHCO3 added After a week the pp is collected and extracted with benzene Cryptopine and protopine separate first from the benzene, and when the filtrate is shaken with NaHCO, laudanosina separates (Hesse, A Suppl 8, 321) It is purified by dis solving in acetic acid, ppg with KI, decom posing the resulting salt with NH, and re crystallising from benzene

Properties—Needles More soluble in ether than thebaine and cryptopine, extremely sol alcohol and chloroform, v sol boiling benzene and ligroin, insol water and alkalis Conc H₂SO₄ (containing ferric salt) gives a brownish red solution, which at 150° becomes green, and inally dark greenish violet FeCl, gives no colour Tastes slightly bitter, its salts have an extremely bitter taste Its alcoholic solution exhibits a strong alkaline reaction Dextro rotatory Its hydrochloride is also dextrorota tory, [a]₁ = 108 in a 2 p c solution at 22 5°

Salts —B'HI laq small prisms, v sl sol cold water, v sol alcohol —B',H PtCl_e 3aq yel low amorphous pp, insol cold water —

B'H2C2O, 3aq prisms, v e sol water

LAUREL OILS The essential oil from the leaves of the common cherry laurel (Cerasus laurocerasus) consists of benzoic aldehyde, HCy, a volatile oil (possibly benzyl alcohol) convertible by oxidation into benzoic acid, and minute quantities of an odorous resin (Filden, Ph. [3] 5, 761, cf. Leger, Ph. [3] 3, 971). The essential oil from the fruits of Laurus nobilis contains a laworotatory terpene C₁₀H₁₆ (164°), S. G. 18 908, a laworotatory sesquiterpene C₁₅H₂₁ (250°), S. G. 18 925, and lauric acid C₁₂H₂₁O, (Blas, A 134, 1, Gladstong, C. J. 17, 1). The essential oil from the leaves of the Californian laurel (Oreodaphne californica) contains terpineol (168°) and umbellol C₂H₁₂O (216°) (Stillmann, B 13, 629).

Laurel-nut oil is a fatty oil, S G 932, derived from Calophyllum inophyllum growing in the East (Hooper, Ph [3] 19, 525)

LAURENE v DI METHYL-ETHYL-BENZENE
LAURIC ACID C₁₂H₂₄O₂ Dodecore acid
Mol. w. 200 [48 6°] (Heintz) (225°) at 100 mm.

(Krafft, B 13, 1415) S G 28 888 (Görgey). H C 1759720 (Louguinne, A Ch [6] 11, 222) Occurs as glyceryl ether in the berries of the bay tree (Laurus nobilis) (Marsson, A Ch 41, 35, Blas, A 134, 1), in the fat of pichurim beans (Sthamer, A 53, 393), in the volatile oil of these beans (Muller, J pr 58, 469), in small quantity in spermaceti (Heintz, A 92, 394), in croton oil (Schlippe, A 105, 14), in the fruit of Cylico daphne sebifera (Gorkom, Tydschrift af neerl Indie, 81, 410), in the so called Dika bread, the fruit of Mangufera gabonensis (Oudemans, J pr. 81, 356), in the age of the Mexicans, a fat obtained from Coccus Axia (Hoppe, J pr 80, 102), and in cocoa nut oil (Görgey, A 66, 303)

According to Schering (A 96, 236) it is among the products of the distillation of cetyl alcohol with potash-lime, but Heintz (A 97, 271) denies this A dodecoic acid (35°], isomeric with lauric acid, may be obtained by treating the amide of myristic acid with Br and NaOH, and converting the resulting dodecylamine into the nitrile and thence into the amide [97°] of dodecoic acid, and boiling the amide with conc

HClAq (Lutz, B 19, 1433)

Preparation—Lauric acid may be obtained from fats containing it by saponification followed by fractional precipitation of the acids by barium acetate (Huntz, A 92, 294, P 92, 429, 583, J pr 66, 1) It may also be obtained from the fat of bay berries by saponifying, distilling the solid fatty acids under reduced pressure, and rectifying in vacuo (Krafft, B 12, 1665)

Properties — Silky needles united in tufts (from alcohol) or scaly crystalline mass (after fusion) Its alcoholic solution has a slight acid reaction It is slightly volatile with steam In sol water, v sol alcohol and ether. Gives di ennyl ketone (C₁₁H₂₅)₂CO when its calcium salt is distilled

Salts—KA' Amorphous S (alcohol) 45 at 15°, 38 at 78° (Oudemans, C C 1863, 737)—KHA'₂ Crystalline S (alcohol) 15 at 15°; 400 at 78°—NaA' White powder S (alcohol) 25 at 15°, 145 at 78°—NaHA'₂. S (alcohol) 2 at 15°—NH₄HA'₂. S (alcohol) 6 at 15°—BaA'₂ crystalline spangles (from alcohol) S 07 at 100°, 0054 at 15° (Oudemans), 009 at 17°, 50 at 100° (Gorgey) S (alcohol) 0187 at 15 , 1009 at 78° (O), 07 in the cold, 5 at 78° (G)—CaA'₂ aq S 0039 at 15°, 0547 at 100° S (alcohol) 0719 at 15°, 220 at 78° (O)—SrA'₂ aq S 0272 at 15°, 220 at 78° (O)—SrA'₂ aq S 0272 at 15°, 036 at 100° S (alcohol) 90 at 15°, 36 at 78°—MgA'₂ 3aq S 023 at 15°—PbA'₂ [110°—120°] (Hentz) S 0011 at 100° S (alcohol) 0047 at 15°, 235 at 100°—CoA'₂ aq—NiA'₂ aq—NiA'₂ 3aq—CuA'₂ S 0023 at 15°, 0029 at 100°—AgA' white powder, consisting of minute slender needles S 0001 at 15°, 0405 at 100°. S (alcohol) 0323 at 15°, 0824 at 78°

Ethyl ether EtA' [-10°] (269°) at 750 mm (Delffs, A 92, 278) SG 20 86 (Gorgey) V L 84 (calc 79) From the acid, alcohol, and HCl

Glyceryl ether C,H,(C,H,D,), (Schiff, B 7, 781) Trilaurn Laurostearn [45°] H. C. 5707420 (Louguinine, A Ch [6] 11, 222). Obtained from bay berries by extracting with alcohol Silky needles, sl sol cold alcohol, v sol ether

Phenyl ether A'C₆H₅ [24½], (210° at 15 mm), pearly plates p-Tolyl-ether A'C₇H, [28°], (220° at

p-Tolyl-ether A'C,H, [28°], (220° a 15 mm) (Krafit a Burger, B 17, 1378)

Amide C₁₁H₂₃ CO NH₂ [102°] (Krafft a Stauffer, B 15, 1729) From the chloride and NH.

Chloride C₁₁H₂₃ CO Cl [-17°] (142½° at 15 mm) Colourless liquid (Krafft, B 17, 1878)

Nutrile $C_{11}H_{23}CN$ [4°] (198° at 100 mm) SG $\frac{1}{4}$ = 835, $\frac{1}{4}$ = 827, $\frac{199}{4}$ = 767 Formed by distilling lauramide with P₂O₈ (Krafft a Stauffer, B 15, 1729) Colourless liquid of peculiar odour

LAURIC ALDEHYDE C₁₁H₂₂CHO [45°] (143° at 22 mm) Prepared by the dry distillation of a mixture of calcium laurate and formiate (Krafft, B 18, 1414) White crystal-

line odourless solid

LAURIN C22H30O3 Bay berry camphor substance discovered by Bonastre (J Ph 10, 32) in the berries of the bay tree, and further ex amined by Marsson (A 41, 329) and Delffs (A 88. 854) It is prepared by boiling the skinned and pounded berries with alcohol of 85 to 90 pc, filtering at the boiling heat, and leaving the liquid to itself for several days Lauro stearin is then first deposited, and on filtering again and leaving the liquid to evaporate, laurin is deposited in crystals contaminated with a viscid oil, from which they may be freed by pressure between paper and recrystallisation Dimetric crystals, destitute of taste and smell, insol water, v sol alcohol, even in the cold, sol ether The solutions are neutral to test papers Laurin does not dissolve in alkalis Laurin can not be distilled without decomposition Its alcoholic solution is not precipitated by acetate of lead or nitrate of silver

LAUROCERÁSIN A name given by Lehmann (N R P 23, 440) to amygdalin when extracted from the leaves of the cherry laurel (Cerasus laurocerasus) or the bark of the berry-bearing alder (Rhamnus Frangula), v Amyg

LAURONE $C_{23}H_{46}O$ is $(C_{11}H_{23})_2CO$ Distribution [69°] S.G. $\frac{70}{4} = 802$, $\frac{100}{4} = 788$ Formed by distilling barium laurate with lime Shining plates (from alcohol) On reduction it gives tricosane (Overbeck, P. 86, 591, A. 84, 289, Krafft, B. 15, 1712)

LAURONOLIC ACID C. H., O. 2 & C. H., CO. H. Formed by distilling camphanic acid, or by heating its barium salt with water at 200°, campholactone is formed at the same time

(Woringer, A 227, 7)

Properties —Oil Sol water and ether Volatile with steam In presence of HCl some of it changes into the isomeric campholactone When distilled with water, a great part changes to the campholactone

Salts—CaA'₂3aq Forms dendritic crystals on the surface of an evaporating solution— AgA'

LAUROSTRARIN v Glyceryl ether of LAURIG

LAUROXYLIC ACID v. DI METHYL BENZOIC ACID.

·LÀUTH'S VIOLET & AMIDO IMIDO IMIDO DI PHENYL SULPHIDE

IAVENDER OIL A volatile oil obtained by distilling the flowers of Lavendula officinalis with steam S G ½ 875 It contains a lavorotatory terpene C₁₀H₁₀ (162°) which forms a crystalline hydrochloride and various oxygenated bodies which yield camphor on further oxidation (Dumas, A Ch 13, 375, Lallemand, A 114, 198, Barth, Z 1867, 509, Bruylants, J Ph [4] 30, 39) English oil of lavender submitted to fractional distillation yields 30 p c of the torpene (176°-186°), and 30 p c of oxygenated products (200°-207°) (Shenstone, Ph [2] 13, 207) LEAD Pb At w 206 4 Mc¹ w not known

LEAD Pb At w 2064 Mc' w not known with certainty, but probably same as at w (v. p 124) [330°-335°] (Brigel, B 6, 191, Pictet, P M [5] 7, 446), [326°] (Riemsdyk, C N 20, 32, Person, J 1849) (Between 14-0° and 1600°) (Carnelley a Williams, C J 35, 565) S G 11 335 at 0° (Quincke, P 97, 396), 11 37 at 0° (Reich, J pr 78, 328), 11 345 to 11 358 at 4°, 11 352 to 11 366 at 23° (Schweitzer, Am Ch 7, 174) S G molten 10 37-10 65 (Roberts a Wrightson, A Ch [5] 30, 181) For other values for S G v Clarke's Table of Spec Gravities [1888], pp 5-6 S H -78° to 11° 03065 (Reg nault, A Ch [3] 26, 286), S H 19° to 48° 0315 (Kopp, Tr '865 71), S H molten 340° to 450° 0402 (Person, A Ch [3] 24, 129) C E 0° to 100° 00002799 (Matthessen, Pr 15, 220) T C (Ag = 100) 85 (Wiedemann a Franz, P M [4] 7, 33) Heat of fusion 5858 (Rudbeig, P 19, 125), 5369 (Person, A Ch [3] 24, 129) E C (Hg at 0° = 1) 48 at 0°, 3 363 at 100° (Lorenz, W 13, 422, 582) Crystallises in regular octahedra For emission spectrum of lead v Werther, J pr 88, 180, Cornu, C R 73, 332, L de Boisbaudran, C R 77, 1152, Hartley a Adency, Tr 1884 63

Occurrence — Lead occurs native in small quantities (eg v Chapman, P M [4] 31, 176, Kokscharow, J M 1875 873, Igelstrom, J M 1889 (i) 32) Galena (PbS) is very widely distributed, the other most important ores of lead are cerusite (carbonate), anglesite (sulphate), pyromorphite (phosphate), and mimetesite (arsenate) Small quantities of oxychloride, chromate, molybdate, tungstate, vanadate, &c, of Pb also occur Lead has been known and used from very early times

Formation—1 PbS is roasted in a reverbe ratory furnace until a portion is oxidised partly to PbO and partly to PbSO₄, the doors are then closed, and the PbS, PbO, and PbSO₂ react to produce SO₂ and Pb, PbS+2PbO=3Pb+SO₂, PbS+PbSO₄=2Pb+2SO₂-2 PbS is roasted in a reverberatory furnace, the temperature being gradually increased until a considerable quantity of PbSO₄ and a little PbO are produced, the doors are then closed, and the temperature is raised until the mass softens but does not melt When the PbS and PbSO₄ react to produce Pb and SO₂ the residue is again roasted, whereby more PbSO₄ is formed, and on raising the temperature with closed doors the PbSO₄ and PbSO₄ relatively to PbS becomes so great that the chief product of their reaction is PbO (PbS+3PbSO₄=4PbO+4SO₂), coal and wood are then thrown into the furnace, and heating is

LEAD 128

continued, when the PbO is reduced to Pb(PbO+C=Pb+CO), at the same time some of the PbSO, is partly reduced to PbS, which, reacting with the remaining PbSO, produces Pb and SO₂ (2PbSO₄+2C=PbSO₄+PbS+2CO₂)—3 PbS is melted with scrap Fe, PbS+Fe=FeS+Pb—4 PbCO₂ is strongly heated with C, PbCO₃+2C=Pb+3CQ—5 PbO is reduced by heating in H or CO, or, with C, KCN, or Na—6 Zinc is suspended in an acidulated solution of a Pb salt, when Pb is ppd on the zinc—7 PbCl₂ is mixed with Na₂CO₂, and heated with KCN or C

Preparation -1 By melting Pb prepared by one of the foregoing methods, exposing the molten mass to a gentle current of air, blowing water vapour through the mass, and running off the metal from beneath the film of oxides of Cu. Sb, Fe, &c, nearly pure Pb is obtained -2 Pb oxalate is strongly heated in a carbon crucible, or is mixed with powdered C and heated -3 Stas prepared pure lead by the following pro cess (Chem Proport 324) Commercial Pb acet ate was dissolved in water, and digested at 40° to 50° in a leaden vessel with sheets of Pb until all Cu and Ag were ppd, the filtered liquid was run into almost boiling water, strongly acidulated with H₂SO₄, the ppd PbSO₄ was very thoroughly washed, and then suspended in a solution of NH, sesquicarbonate and NH, until transformed into PbCO, the PbCO, was thoroughly washed, a part of it was decomposed to PbO by heating in a Pt dish, and the rest was almost, but not quite, entirely dissolved in dilute HNO, Aq, the solution of Pb(NO,) was heated to boiling, and the PbO was added little by little, the last traces of he were thus ppd as oxide, the boiling liquid was filtered and poured into solution of NH, sesquicarbonate In this way pure PbCO. The PbCO, was dried, and added was obtained little by little to pure molten KCN contained in an unglazed porcelain crucible placed within a larger crucible, the space between being filled with powdered Al₂O₃ previously heated and mixed with 5 pc meited and powdered borax The Pb thus obtained was again placed in pure molten KCN, and kept there until the upper surface of the Pb appeared convex and lustrous like pure Hg, after partial cooling the Pb was run off into a mould of polished steel If a trace of PbO or PbS is present in the molten Pb the surface does not become convex

Properties -Almost white, lustrous metal Ordinary lead is blue grey, it contains traces of Ag, Cu, Sb, and sometimes Fe and Mn malleable and ductile, but the properties are greatly affected by small quantities of impurities, notably by PbO, which is somewhat soluble in molten Pb Tenacity very low Somewhat so-Leaves a mark on paper Lead 1s so soft that it can be cut by a knife or scratched by the nail, traces of foreign metals, or of As or S, increase the hardness of Pb By slowly cooling molten Pb, piercing a hole in the crust by an iron rod, and pouring off the still molten portion, the metal is obtained in regular octahedra often ag gregated together similarly to crystals of NH,Cl (Marx, S 57, 193, Stolba, D P J. 164, 371) Crystals of Pb are also obtained by hanging a rod of zine in a slightly acidulated solution of a Pb salt, or by passing an electric current through

such a solution Pb vaporises at high tempera tures (1400° 1600°), the vapour is very poisonous. The lustrous surface of Pb quickly tarnishes in ordinary air from formation of a film of oxide (probably Pb₂O) Very finely divided Pb is quickly changed to the suboxide Pb.O. such finely divided Pb may be obtained by covering a Zn plate with a little PbSO, made into a paste with water, laying another Zn plate on the top, and placing the whole in NaClAq for 9 or 10 days (v Bolley, Ph C 1850 59) Pb is readily changed to PbO on the surface by melting in air Pb is not changed in dry air, nor when kept under pure water from which all air has been removed, in contact with water and the atmosphere it becomes gradually covered with a white deposit of 2PbCO3, PbO2H2, and small quantities of a soluble Pb salt are also formed (v Reactions, No 2) Pb is soluble in HNO₃Aq, and is slowly changed to PbCl₂ by the action of HClAq in the air, hot conc H2SO, forms PbSO, Pb is oxidised by heating with KNO, or KHSO. Combines with the halogens, also with S, Se, P, and

As, forms alloys with many metals

The atomic weight of Pb has been determined
(1) by finding V D of PbCl₂ (Roscoe, Pr 27, 426),
and analyses of this compound (Marignac, Ar Sc
1, 59, 209, Dumas, A Ch [3] 55, 196), (2) by
syntheses of Pb(NO₃)₂ and PbSO₄ (Stas, Rech
101, Chem Proport 329), (3) by converting
Pb, PbO, and PbS into PbSO₄, and by analysing
PbCO₃ (Berzelius, P 8, 15, G A 37, 259, 265,
Turner, A 13, 17), (4) by determining S H of

Pb (Regnault, A Ch [3] 26, 286)

Lead is metallic in its chemical behaviour The oxide PbO is strongly basic, it is slightly soluble in water, and the solution turns red lit mus blue and absorbs CO₂ from the air, it de composes hot solutions of NH, salts with evolu tion of NH2, and it reacts with acids to form salts PbX_2 (X = NO_{3} , ${}^{1}_{2}SO_4$, &c), $PbCO_3$ is isomorphous with the carbonates of the alkaline earths, on the other hand, PbO dissolves in fairly conc KOHAq, probably forming a salt PbO,K, and compounds of PbO with CaO and Ag,O are PbO₂ reacts with strong bases, eg KOH, to form unstable salts, eg K.PbO₃, on the other hand, treatment of Pb₂O₄ with conc H,PO,Aq or H,CO,Aq produces solutions which react as if they contained salts of PbO2. The greater number of the lead salts correspond with the oxide PbO, Pb(CH₃)₄, however, is stable as a gas

Lead is placed in Series II of Group IV , the other odd series members of this group are Si, Ge, and Sn Pb more nearly resembles Sn than any other member of Group IV, it is more distinctly metallic than the other elements of the group, the other elements of this group form several compounds MX^t₄, whereas most of the Pb compounds belong to the form MXI. Pb forms many basic and several double salts (cf CARBON GROUP OF ELEMENTS, vol 1 p 684, also Tin group of elements, in vol 1v) In its physical properties Pb resembles Tl, one series of Tl salts, however, is similar to those of the alkalı metals, and the other senes resembles those of the earth metals (v EARTHS, METALS OF The atom of Pb is divalent THE, vol 11 p 424) in the gaseous molecule PbCl2, and tetravalent in the gaseous molecule Pb(CH₂)4.

124 LEAD.

Ramsay (C J 55, 521) has determined the lowering of vapour pressure of Hg produced by dissolving Pb in Hg, the results obtained make it probable that the molecular weight of lead is the same as the atomic weight, this result assumes the accuracy of Van't Hoff's law, that equal volumes of dlute solutions contain equal numbers of molecules of the dissolved substances, and it also regards the molecular weight of liquid Hg as the same as the atomic weight

Reactions —1 Unchanged in dry air, super ticially oxidised (probably to Pb,O) in moist air, oxidised to PbO by heating in air or oxygen -2 Water quite free from air has no action on Pb at ordinary temperatures (Stalman, D P J 180, 366, Bottger, J 1866 232, but v Muller, J pr [2] 36, 317) Water and arr together dis-J pr [2] 36, 317) solve a little Pb, and at the same time a deposit of 2PbCO₃ Pb(OH)₂ is formed Water charged with CO2 under a pressure of a few atmo spheres dissolves considerable quantities of Pb (perhaps in the form of an acid carbonate) The presence of small quantities of nitrates, espe cially NH, NO₃, of soluble alkaline chlorides, and of some other salts, eg (NH₄)₂SO₄, increases the solvent action of water on Pb, the amount of Pb in solution is greater after a few days' action than after many days' exposure to the air In these reactions the soluble salt of Pb is probably slowly acted on by the CO2 of the air with formation and ppn of insoluble 2PbCO, Pb(OH), The presence of alkaline carbonates or of a little Ca silicate in water almost wholly stops the solvent action on Pb, probably the insoluble hydrocarbonate is formed as quickly as Pb is dissolved The action of water on lead has been examined by Graham, Miller a Hofmann, Noad (C J 4, 20), Yorke (P M [3] 5, 82), Dumas (C R 77, 1054), Berthelot (C R 77, 1063), Pattison Muir (C N 25, 294, 33, 102, 125, 145, 34, 223, 234, 35, 82, 110, C J 31, 660), Muller (J pr [2] 36, 317), Carnelley a Frew (S C I)7, 15, 78), and others Granulated lead slowly decomposes boiling water, evolving H (Stolba, J pr 94, 113) -3 Lead is dissolved by several acids, slowly by hot cone HClAq in contact with air, also slowly by conc H SO, (Calvert a Johnson, C J 16, 66), rapidly by HNO, Aq For account of gaseous products of neaction with HNO, Aq v Ackworth a Armstrong, C J 82, 54.

Technical applications of lead—Lead is largely used for vessels and apparatus in which different chemical processes are conducted, e.g. for sulphuric acid chambers, water pipes are usually made of lead. Alloys of lead with tin form solder and pewter, an alloy with As is used for making shot, an alloy with Sb is used as type-metal, and emery wheels and grinding tools used by lapidaries are made of an alloy of Pb and Sb, alloys of Pb with Sn and Bi have low melting-points. Lead oxide, chromate, accetate, and carbonate are all largely used in manufactures.

Detection and Estimation—HClAq ppts white PbCl₂ from solutions of Pb salts, sl sol cold water, fairly sol hot water, nearly insol dilute HClAq Dilute H₂SO₄, or a soluble sulphate, ppts white PbSO₄ almost insol dilute H₂SO₄Aq, quite insol alcohol. K₂CrO₄Aq ppts

yellow PbCrO,, insol water KIAq ppts yellow PbL, sol boiling water, but reppd in yellow crystalline spangles on cooling H₂S ppts brownish black PbS, insol dilute acids, alkalis, or alkaline sulphides, presence of much HCl prevents ppn from rather dilute solutions of salts of lead, in presence of a little HCl pp is sometimes red or vellow red, and consists of xPbS yPbCl₂ (v Lead sulphochloride of) The H₂S test is said to detect 1 pt of lead in 100,000 pts of water, the H₂SO, test 1 pt in 20,000, and the K₂CrO, test 1 pt in 70,000 Pb may be estimated as Pb₂O, by ppn with dilute H₂SO₄Aq adding about 2 vols of alcohol, washing with alcohol, drying and callining

Supposed clotropic form of lead When lead is deposited on the negative electrode by passing a current through a neutral or acid solution of a lead salt, and the current is con tinued for some hours, the lead becomes the colour of copper (Wohler, A Suppl 2, 135) After washing the red leaflets thus obtained with water and alcohol, they retain their colour on exposure to the air, and are not acted on by dilute HClAq or cold dilute HNO,Aq, or alkalis, but are readily dissolved by hot HNO3Aq, heated in H they melt above 200° and become ordinary lead Wöhler regarded the red substance either as an alloti pic form of lead, or as a hydride of lead, Stolba (J pr 94, 113) suggested that the red colour was due to a film of oxide on the surface of the lead (v also Schutzenberger, C R86, 1265)

Lead, alloys of Lead alloys with many metals, the alloys are produced by fusing together the constituent metals, some of them are definite compounds, in these cases either of the constituents is generally soluble in the compound

Alloys with bismuth, and with bismuth and other metals. Pb and Bimay be alloyed in all proportions, mall-ability is diminished by adding more than an equal weight of Bi By fusing together 70 pc. Pb, 15 pc. Bi, and 15 pc. Sb an alloy is obtained which expands on cooling. An amalgam of Pb (4 pts.) Bi (2 pts.), and Hg (1 pt.) may be melted by rubbing pieces of it together. Alloys of Pb with Bi and Sn are known as fusible alloy, the MP varies from c. 90° to c. 170°, all these alloys are said to solidify at 98° (For MP and solidification points of these alloys v. Dallo, C. C. 1865. 831, for expansion and S. H. v. Spring, A. Ch. [5]. 7, 178, also Wiedemann, W. 3, 237, for thermal conductivity v. Wiedemann a. Fianz, P. 89,514, 108, 399, cf. also vol. 1. p. 511)

Britannia metal is composed of equal parts of brass, Sn, Sb, and Bi, Queen's metal of 1 pt Pb, 1 pt Bi, 1 pt Sb, and 9 pts Sn Alloys of Pb with Bi, Sn, and Ag are very fusible, melting as low as 45°, the alloy often used for tinning the inside of glass globes, tubes, &c is made by fusing together 1 pt Pb, 1 pt Sn, 2 pts Bi, and adding 10 pts Ag

Alloys with copper v vol ii p 254

Alloys with mercury Pb easily amalgamates with Hg, by rubbing together Pb filings with Hg or by adding Hg to molten Pb An amalgam containing 33 pc Pb is liquid, an amalgam of equal parts Pb and Hg can be crystallised Contraction occurs during the amalgamation

Alloys with potassium and solium Prepared either by directly heating the metals together or by fusing PbO with an alkaline flux, eg with cream of tartar When distilled with EtI, MeI, &c, compounds of Pb with Et, Me, &c are obtained

These metals may be Alloys with tin alloyed in all proportions, the SG of the alloy is always a little less than that calculated from the SG of the constituents There are no indications of the formation of definite com pounds (v Laurie, C J 55, 677) These alloys are very easily ignited and burnt The two com monest alloys of Pb and Sn are solder and pewter Fine solder contains 1 pt Pb and 2 pts Sn, common solder, equal pts Pb and Sn, coarse The M P varies solder, 2 pts Pb and 1 pt Sn from c 340° for 1 pt Pb and 2 pts Sn, to 370° for equ l parts Pb and Sn, and 440° for 2 pts Pb and 1 pt Sn, by increasing the relative quantity of Pb the MP rises until the alloy of 25 pts Pb to 1 pt Sn melts at c 560°, by increasing the relative quantity of Sn, above 2 pts to 1 of Pb, the MP also slightly rises until the alloy of 6 pts Sn to 1 pt Pb melts at c Pewter is an alloy of c 80 pts Pb with According to Rudberg (P 18, 20 pts Sn 240) when Pb and Sn are melted together and allowed to cool, the thermometer always shows a stationary point at 187°, he thinks that a compound PbSn₃ is always formed, that this alloy has a fixed solidification point lower than that of Pb (326°) or Sn (228°), and that the heat produced by the solidification of this alloy acting on the excess of Pb or Sn causes fluctuations in the final solidification point of the whole mixture (v also Pohl, WAB 1850 402, Riche, CR55, 143, Wertheim, P Erganzbd, 2, 75, Matthicssen, P 130, 62) It seems that the amount of Pb in pewter vessels for domestic use should not exceed 18 p c, else Pb may be dissolved out by the action of dilute acids, e g vinegar

Alloys with tin and copper metal is an alloy of 43 pc Pb, 80 pc Cu, 101 pc Sn, and 5 6 pc Zn A little Pb is sometimes added to Cu and Sn in making bronze

Alloys with palladium A crystalline, greyish white, brittle alloy is obtained by fusing granulated Pb with rather more than its own weight of Pd foil, and removing excess of Pb by the action of acetic acid and CO, The alloy has the composition PdsPb, SG 11 225 (Bauer, B 3, 691, 4, 419)

Alloys with platinum Analloy having the composition PtPb is formed by fusing 3 pts Pb with 1 pt Pt, and exposing the product to the prolonged action of Co., action of the prolonged action of the state of the to the prolonged action of CO₂, O, and acetic Steel-Bauer (lc) also describes an alloy PtPb2

Alloys with zine Pb and Zn alloyin all proportions, all the Zn is removed by heating Alloying Pb with Zn increases if the Pb Alloys of Pb, Zn, and very strongly the hardness of the Pb Sn solidify at 168°, when the ratio is 2Pb Zn 9Sn the alloy solidifies at 168° only, but other alloys show also two higher points

Lead also alloys with chromium and man

Lead, antimonate of, v vol 1 p 286

Lead, antimonides of Pb and Sb may be melted together in all proportions, the alloys are crystalline, most of them are formed with expansion Ordinary type metal consists of 83 pts Pb and 17 pts Sb (v Riche, C R 55, 143, Matthiessen, P 110, 28, Calvert a Johnson, P M [4] 18, 354, H v d Planitz, B 7, 1664, Rollmann, P 84, 277)

Lead, arsenates of, v vol 1 p 308 Lead, arsenates of Pb melted with As takes up c 16 pc of the latter, the alloys are brittle and very fusible, some, but not all, of the As is expelled by heating Shot metal is an alloy of Pb

with not more than 3 p c As

Lead, arsenites of, v vol 1 p 306

Lead, borates of, v vol 1 p 530 Lead, borofluoride of $Pb(BF_4)_2[=PbF_2 2BF_4]$ Prismatic crystals, obtained by dissolving PbO in excess of HBF, Aq and evaporating to a syrup Crystallises with difficulty, partially decomposed by water or alcohol (Berzelius, P 2, 113, cf.

Lead, bromide of PbBr₂ Mol w not certain, but from analogy of PbCl is probably 365 9(= PbBr) Melts at c 499° (Carnelley, C J 33, 278), boils at c 861° (Carnelley a Williams, C J 33, 283) SG ppd PbBr₂ 6 572 at 19 2° (Clarke's Table of Specific Gravities [1888] 32) $\dot{H} F [Pb,Br'] = 64,450$, [Pb,Br',Aq] = 54,410 (Th. 3, 337) Obtained by digesting PbO or PbCO. with HBrAq, or by ppg the solution of a Pb salt by HBrAq or a soluble bromide Obtained in well formed, colourless, rhombic needles by slowly evaporating a solution of Pb in alcohol containing Br (Hjortdahl, Z K 3, 302) containing Br (Hjoitdahl, Z K 3, 302) Sl sol. cold, more sol hot, water, more sol acids From the solution in hot cone HBrAq (72 pe HBr), Ditte says that white lustrous needles, PbBr₂ 3H₂O, crystallise (C R 92, 718), and that the compound 5PbBr 2HBr 10H2O is obtained by passing HBr into the solution of PbBr, in HBrAq After melting, PbBr₂ solidines to a yellow, horn like mass Heated in air, a yellow yellow, horn like mass mass remains containing the orybromide Pb OBr₂ (= PbBr...PbO), the same oxybromide is obtained by digesting PbBr with Pb(C H,O2).Aq A compound of PbBr, with PbCl, has been ob tained, also compounds of PbBr, with PbI2, and with Pb(CNS), (1 Lead, bromochloride of, Lead, woodbromides of, and Lead, bromosul-André (A Ch [6] 3, 104) phocyanides of) describes several double compounds of PbBr. with NH,Br

Lead, brom iodides of, v Lead, iodobrom rdes of

Lead, bromochloride PbBr, PbCl, (=PbBrCl)White needles, observed by Iles in a blast furnace where lead carbonate ores had been reduced (C N 43, 216), crystallisable from water, SG 5741

Lead, bromosulphocyanides of

PbBr, Pb(CNS), brownish crystals, by digesting the constituents together, and then crystallising from boiling water By acidifying with HBrAq, the salt 8PbBr Pb(CNS)2 is produced (Grisson a Thorp, Am 10, 229)

Lead, chlorides of Only one chloride of lead, PbCl., has been isolated, but there is strong proof of the existence of the tetrachloride, PbCl4, in solutions of PbO2 in HClAq

LEAD CHLORIDE, PbCl2. (Lead dichloride

Plumbous chloride Horn-lead) Mól w 277 14 8 G 5 805 at 15° (Stolba, J pr 97, 503), 5 88 (Brugelmann, B 17, 2359) V D 187 1 at c 1080° (mean of 4) (Roscoe, Pr 27, 426) Melts at 498°, and boils between 861° and 954° (Carnelley, C J 33, 278, and C a Williams, C J 35, 564) Crystallises in rhombic system, a b c = 5948 1 5949 (Schabus, W A B 1850 456) H F [Pb,Cl²] = 82,770, [Pb,Cl²,Aq] = 75,970 (Th 3, 337)

Occurrence —As cotumite, found in the crater of Vesuvius after the eruption of 1822,

mixed with NaCl and CuSO.

Formation —1 By heating Pb in a stream of Cl, combination occurs slowly —2 By dissolving Pb in hot HClAq in contact with air, PbCl, separates on cooling —3 By adding solution of a chloride, eg NaClAq, to a cone solution of a Pb salt —4 By dissolving PbS in hot HClAq and crystallising

Preparation —PbO or PbCO, is boiled with dilute HClAq, and HClAq is added little by little until all is dissolved, the liquid is allowed to cool, and the PbCl, which separates is repeatedly

crystallised from boiling water

Properties — Large, white, rhombic crystals (v supra), which melt at 498° and boil between 861° and 954° (v supra) VD atc 1080° agrees with the formula PbCl₂ Sl. sol cold water, S = 95 at 165°, solution contains 9414 pc PbCl₂ (Bell, C N 16, 09), addition of 1 pc HCl. diminishes S to 347, and with 14 pc HCl is present S increases, S in HClAq S G 1162 = 29 (Bell, C c) According to Field (C J [2] 11, 575) PbCl₂ is less soluble in NaClAq containing 5 pc NaCl than in water (S = 23), but the values of S for water and cone NaClAq are about the same The considerably greater solubility of PbCl₂ in cone than in dilute HClAq is supposed by Ditte to be due to the formation of a compound of PbCl₂ and HCl which is decomposed by water (C R 92, 718) Ditte gives the following table —

HCl in 100 pts H _s O	PbCl _a dissolved in 1000 pts of the liquid in col 1				
0 56 10 18 21 9 81 5 46	at 0° 8 2 8 1 2 2 4 4 7 11 9 29 8	20° 11 8 3 1 4 4 8 6 2 14 1 30 (at 17°)	40° 17 46 32 72 104 19	55° 21 65 55 98 129 24	80° 31 12 4 12 19 8 23 8 38

PbCl₂ is readily dissolved by boiling water, but almost all crystallises out on cooling Insol alcohol 94 pc, somewhat sol in more dilute Fairly sol Nac,H₂O₂Aq, Na,S₂O₃Aq, and some other salt solutions After melting and cooling, PbCl₂ appears as a horn-like mass (hence the uame horn-lead formerly used)

Reactions—1 Heated in the air until white fumes cease to come off, a light yellow onythionide Pb₂OCl₂ (=PbCl₂PbO) is formed (v. Lead, oxychlorides of)—2 Recently ppd PbCl₂ when digested with cold neutral lead acetate produces an oxychloride 2Pb₂OCl₂H₂O (Brandes, A. 10, 273)—3. The oxychloride

Pb₂OCl₂·H₂O is obtained by partially ppg PbCl₂Aq by time water —4 By adding caustic potash to PbCl₂ suspended in water, the oxy chloride PbCl₂ 2PbO is said to be formed (Ditte, C R 94, 1180) —5 According to Berzelius, the product of the action of ammonia on PbCl₂ is PbCl₂ 3PbO 4H₂O —6 Heated in carbon mon oxide, COCl₂ and Pb are produced —7 Heated, not too strongly, in phosphoretted hydrogen, HCl, P, and Pb are formed —8 Oxidised by alkaline hypochlorites to PbCl₂—9 Long continued passage of Cl into PbCl₃ suspended in water most probably produces PbCl₄, PbO₂ being simultaneously ppd (v bisher, C J 35, 284)

water most probably produces PbCl, PbO, being simultaneously ppd (v I isher, C J 35, 284)

Combinations—1 PbCl₂ absorbs ammonia gas, forming 2PbCl₂ 3NH₂ according to H Rose All the NH, is readily given off on warming -2 Combines with lead monoxide, when the two are heated together, to form oxychlorides $x \operatorname{PbCl}_2 y \operatorname{PbO}$ (v Lead, oxychlorides of)— 4 With lead carbonate forms PbCl₂ PbCO₃, ob the teat the two salts, or by the action of CO_2 on $PbCl_2$ under pressure (Miller, C J [2] 8, 37) -5 With lead acetate to form $PbCl_2$ pbCl₂ with $Pb(C_2H_3O_2)_2$, obtained by mixing freshly ppd $PbCl_2$ with $Pb(C_2H_3O_2)_2$ and enough glacial acetic acid to form a viscid mass, which soon solutions and removing excess of each by soon solidifies, and removing excess of acid by pressure (Carius, A 127, 87)—6 With lead phosphate, forms PbCl₂ Pb₃(PO₄)₂ H₂O and PbCl₂ 2Pb₃(PO₄)₂, or according to Gerhardt (A Ch [3] 22, 505) PbCl₂ Pb₂H (PO₄) The former is produced by pouring boiling PbCl,Aq into excess of boiling Na₂HPO₄Aq, the latter by pouring the Na phosphate into the PbCl₂ solution (Heintz, P 73, 122) Pyromorphite PbCl₂3Pb₃(PO₄)₂ occurs native -7 Combines with lead bromide to form PbCl₂ PbBr, with lead volude to form PbCl₂ PbL₂, with lead fluoride to form PbCl₂ PbF₂, and with lead sulphocyanide to form PbCl₂ PbC(NS)₂ (v Lead bromochloride, Lead volobromides, Lead volobromides, Lead chlorofluoride, and Lead chlorosulpho cyanide) -8 Probably combines with chlorine to form PbCl₄, when Cl 18 passed into PbCl₂ dissolved in considerable excess of HClAq, or when Cl is passed into PbCl,Aq mixed with CaCl₂ (v Lead tetrachloride) — 9 André (A Ch [6] 3, 104) describes various double compounds of PbCl2 with NH4Cl

LEAD TETRACHLORIDE (Plumbuc chloride)
No other chloride of lead except PbCl₂ has been
solated, but there is considerable evidence in
favour of the existence in HCl solution of tetra

chloride PbCl

If a considerable quantity of HClAq is added to PbCl₂, and Cl is passed in, the PbCl₂ dis solves to a reddish brown liquid, on warming Cl is evolved, addition of water causes ppn of PbO.

A mixture of PbCl₂Aq with CaCl₂Aq absorbs much Cl and forms a deep yel'ow liquid, which may be preserved unchanged in a closed vessel, but is decomposed in an open vessel giving PbCl₂ and Cl, a few dr-ps of this liquid added to a large quantity of water gives a pp of PbCl₂ and PbO₂, alkalis and alkaline carbonates ppt PbO₂, MnCl₂Aq ppts MnO₂ and PbCl₂, Fe, Cu, Zn, gold leaf, and finely divided Pt, are soluble in the liquid with separation of PbCl₂, it rapidly oxidises many organic bodies, PbCl₂ being ppd.

(Sobrero a Salmi, A Ch [8] 29, 165, Nucklès,

A Oh [4] 10, 323)

PbO₂ dissolves in cold fairly cone HClAq From this yellow solution, alkalis, alkaline carbonates, oxides and carbonates of Ba, Mg, Zn, &c , and alkaline borates and acetates, ppt PbO, The solution smells of Cl, and is decomposed by heat with evolution of Cl and ppn of PbCl2 If the HClAq is saturate. with PbO₂ the addition of water ppts PbO₂ Fisher (C J 35, 282) determined the ratio of Pb ppd from this solu tion by water as PbO₂ to Cl given off by decomposing the solution with ppn of PbCl₂ The ratio was almost exactly Pb 2Cl, now this is the ratio required on the hypothesis that the decomposition by water proceeds as shown in equation (1), and the decomposition to PbCl2 and Cl proceeds as shown in equation (2)-

(1)
$$PbCl_4 + 2H_2O = PbO_2 + 4HCl$$

(2) $PbCl_4 = PbCl_2 + Cl_2$

Fisher proved that the whole of the Pb in solution is thrown down by water as PbO₂ A yellow liquid with properties the same as those of the liquid just described is obtained by treating Pb.O. with a considerable quantity of HClAq

(Fisher, lc)

By the method described above, Sobrero a Salmi (lc) obtained a double salt PbCl, 9NaCl, and Nickles (lc) obtained PbCl₄ 16C₆Cl₂ Lva poration in vacuo, over conc KOHAq, of a solu tion of PbO2 in HClAq produces crystals of PbCl2 containing some PbCl, according to Bendant a Daguin (Ann M [5] 4, 239, v also Nikolukine, J R 1885 207, abstract in C J 50, 123)

Lead, chlorobromide of, v Lead, bromo-

thloride of

Lead, chlorocarbonate of, v Lead chloride, Combinations No 4

Lead, chlorocyanide of, v Lead cyano

chloride of

Lead, chlorofluoride of PbCl PbF, (=PbFCl) Obtained by ppg boiling PbCl₂Aq by KFAq, or Pb(C.H.O.) Aq by a solution of 2 parts NaF with 3 parts NaCl (Berzelius) A white powder, slightly soluble in water without decomposition

Lead, chloriodides of, v Lead, vodo-

chlorides of

Lead, chlorophosphate of, v Lead chloride, Combinations No 6

Lead, chlorosulphide of, v Lead, sulpho-

chloride of

Lead, c' lorosulphocyanide of,

PbCl, Pb(CNS), by digesting the constituents together, and crystallising from boiling water, slowly changed to PbO₂H₂ by NH₃Aq (Grisson a. Thorp, Am 10, 229)

Lead, chromates of, v vol 11 pp 155 and

Lead, cyanides of None has been isolated, but an oxycyani'e, and also ferri- and ferro cyanides, are known, v vol 11 pp 341, 339, and 335

Lead, cyanochloride of PbCl, 2PbCy, digesting PbCl₂ with KCyAq (Grisson a Thorp, Am 10, 229)

Lead, ferricyanide of, v vol n p 339 Lead, ferrocyanide of, v vol 11 p 335 Lead, fluochloride of, v Lead, chlorofluoride of.

Lead, fluoride of PbF₂ Pb is not acted on by HFAq, PbO2H2, or PbCO3, dissolves in HFAq, and on evaporating, and heating to remove HF. PbF₂ remains PbF₂ is also ppd on adding Pb($C_2H_2O_2$)₂Aq to HFAq A white powder, slightly soluble in water, sol in HNO₂Aq (Berzelius) Gunz (A Ch [6] 3, 5) gives HF of PbF_2 as $[PbO^2H^2, 2HF] = 24,300$

Lead, hydroxides of, v Lead, oxides and

hydrated oxides of

Lead, iodide of PbI₂ Mol w not certainly known, but from analogy of PbCl2 probably 459 46 (= PbI₂) S.G 6 12, 5 6247 molten at 383° (Rodwell, T 1882 1144) Melts c 383°. and boils between 861° and 954° (Carnelley, C J 33, 277, C a Williams, C J 37, 126) For ex pansion of PbI₂ v Rodwell, Pr 32, 23 HF [Pb,I'] = 39,800 (Th 3,337)

Preparation --Solution of Pb(NO₂)₂ is added to solution of FeI, the pp is washed with cold water and dried KI or CaI, may be used instead of FeI₂. If Pb(C₂H₃O₂)₂Aq is added to KIAq oxylodides are formed when excess of Pb salt is added, and soluble double rodides are formed if excess of KI is present, to prevent both results the solution of Pb(C₂H₁O₂)₂ should be

acidified either with HNO, or $C_2H_1O_2$ Properties and Reactions — Golden yellow crystals, hexagonal, ac=1 1 3018 (Nordenskjöld) Melts when heated to a brown red liquid. and solidifies to a yellow mass Heated in the arr I is evolved, and oxylodides (q v) are formed Decom S cold water 03, boiling water 515 Zn or Fe boiled with PbI2 under posed by Cl water forms ZnI₂ or FeI₂, and ppts Pb Na₂S₂O₃ in excess forms Pb sulphite and NaI (Michaelis a Koethe, B 6, 999) NH, Aq added to boiling PbI,Aq ppts 3PbO PbI, 2H,O Dry PbL 1s unchanged by light, when moist and exposed to direct sunshine, in contact with the air, it is slowly changed to PbCO₂ and PbO₂ with separa tion of I, this change is hastened by all substances which absorb I (Schmid, P 127, 493) PbI, is somewhat soluble in conc solution of alkalı iodides, but is ppd on dilution

Combinations -1 Absorbs ammonia, form ing a white compound PbI, 2NH, -2 With lead monoxide forms various oxylodides xPbI2yPbO (v Lead, oxyrodides of) -3 By dissolving PbI2 in warm todhydric acid solution, and allowing to cool, white lustrous needles of PbL 2HI = H2PbL separate This compound may be called sodo plumbhydric acid or sodo plumbic acid, it is decomposed by water, gives off HI in vacuo, according to Berthelot, the crystals contain 10H₂O (C R 91, 1024)—4 PbI₂ combines with potassium iodide to form various double salts, one of which, PbI, 2KI, seems best regarded as the K salt of H.PbI. Yellow, lustrous leaflets of PbI, KI are obtained by dis solving the constituent salts in the ratio PbI₂ KI in boiling water, and allowing to cool, by dis solving this salt in warm KIAq and cooling, the salt PbI, 4KI is said to be obtained in white needles (Boullay, A Ch [2] 34, 366) Remsen (Am 11, No 5) asserts that the process de scribed by Boullay does not result in production of PbI, 4KI, and that the salt formed with most case when PbI, and KI react under different conditions is PbI2 KI H2O (cf Ditte, C R 92) 1 1841) -5 By mixing a boiling solution of KI

and NH₄Cl with Pb(C₂H₂O₂)₂Aq, taking care that | Pb₂O is prepared by heating PbC₂O₄ in a retort no permanent pp was formed, and cooling, Völkel obtained clear yellow lustrous needles of PbI₂ 2NH₄Cl (P 62, 252), decomposed by water with separation of PbI₂ By saturating hot NH4ClAq with PbI2, cooling, pouring off from PbI₂ 2PbCl₂ which separates, and evaporating, Poggiale (C R 20, 1180) obtained PbI₂ 4NH,Cl 2H₂O, decomposed by water with separation of PbI₂—6 PbI₂ combines with silver codide For properties of the PbI₂ AgI produced v Rodwell (Pr 32, 540), Bellati a Romanese (Pr 34, 104) -7 Compounds with lead bromide are formed by crystallising PbI₂ from HBrAq (v. Lead, vodobromides of)—8 Compounds with lead chloride, PbI₂ PbCl₂(=PbICl) and PbI₂ 2PbCl₂, are known (v. Lead, vodochlorides of)—9 By boiling PbCO₃ repeatedly with PbI₂Aq, Poggiale (C R 20, 1184) obtained PbI₂PbCO₃ — 10 PbI₂Pb(C₂H₃O₂)₂ was obtained by Carius (A 127, 87) similarly to the PbCl₂ compound (v Lead chloride, Combinations No 5)

Lead, 10dobromides of By crystallising PbI2Aq from HBrAq, Grisson a Thorp obtained the compounds (1) PbBr₂ PbI₂, (2) 3PbBr₂ PbI₂,

(3) 6PbBr₂ PbI₂ (Am 10, 229)

Lead, iodocarbonate of, v Lead, vodide of,

Combinations No 9

Lead, iodochlorides of The compound PbClI (= PbCl₂.PbI₂) is obtained, in sulphur yellow prisms, by cooling a solution of PbI2 in boiling HClAq (Labouré, J Ph [3] 4, 328) According to Engelhardt the compound contains more PbI2 than required by the above formula (J pr 67, 293) By saturating hot NH, ClAq with PbI₂, and allowing to cool, Poggiale obtained yellow needles of PbI₂ 2PbCl₂ (C R 20,

Lead, 10dosulphocyanide of, PbI₂ 3Pb(CNS)₂, formed with some difficulty by digesting the constituents and crystallising from hot water

(Grisson a Thorp, Am 10, 229)

Lead, oxides and hydroxides (or hydrated oxides) of Five oxides of lead have been isolated, viz, Pb₂O, PbO, Pb₂O₃, Pb₃O₄, and PbO₂, one or more oxides intermediate between Pb₂O₄ and PbO₂ perhaps exist Two hydrates of PbO, viz 2PbO H,O and 3PbO H,O are known, the hydrates Pb₂O₃ 3H₂O and PbO, H₂O have also been isolated. The most stable oxide is PbO, Pb₂O is easily oxidised to PbO by heating in air, and Pb2O3, Pb3O4, and PbO2 are reduced to PbO when strongly heated PbO reacts with acids as a basic oxide, forming salts PbX2, X=NO₅, Cl, \$SO₄, \$PO₄, &c, it decomposes NH₄ salts, evolving NH₃, and combines with CO₂ to form PbCO, PbO also reacts with strongly basic oxides as an acidic oxide forming unstable plumbites, e g K2PbO2 PbO reacts as an acidic peroxide, with KOH and NaOH it forms fairly stable plumbates, Mr₂PbO₃, with most acids it forms salts of PbO, but it appears capable of dissolving without reduction in glacial acetic and phosphoric acids The reactions of Pb2O2 and Pb.O. indicate that these oxides are compounds of the form xPbO yPbO₂ As none of the oxides of Pb has been gasified the molecular weight of none is known with certainty

LEAD SUBOXIDE, Pb2O The grey pellic's which forms on the surface of lead exposed to the air consists of Pb₂O, according to Berzelius

to near 300° as long as any gas is given off, 2PbC₂O₄ = Pb₂O + CO + 8CO₂, the residue is allowed to cool in the retort (Dulong, S 17, 229, Pelouze, J pr 25, 486) Pb₂O is a black powder, S G 9772 (Playfair a Joule, C S Mem 8, 83), heated in air it burns to PbO, heated out of contact with air, PbO and Pb are produced Moist Pb2O rapidly absorbs O from the air, forming white PbO x11,O Dilute acids resolve Pb₂O into PbO, which dissolves, and Pb, saturated Pb2NO₃Aq produces a similar resolution, but Pb₂O is wholly soluble in dilute Pb2NO₃Aq This oxide was at one time supposed to be a mixture of PbO and Pb, but this is disproved by the facts that when the oxide is rubbed with Hg either dry or under water, no Pb is removed, and that PbO is not removed from it by boiling with Pb acetate solution

LEAD PROTOXIDE PbO (Plumbous oxide Litharge Massicot) Mol w unknown, oxide has not been gasified SG 9 277 at 17 50 (Herapath, P M 64, 321), 925 (Playfar a Joule, C S Mem 3, 84), 917 to 988 (Ditte, C R 94, 1310), 874 to 929 (Geuther, A 219, 60) HF [Pb,O] = 50,300, heats of neutralisa $[PbO, 2HClAq] = 56,830, [PbO, HNO^3Aq]$ = 24,250 to form basic nitrate (Th 3, 337) Crystallises in rhombic forms $a \ b \ c = 666 \ 1 \ 971$ (Nordenskjold, P 114, 619, v also Mitscherlich, P 49, 403, J pr 19, 451, Graulch, W A B 28, 282, Marx, J pr 3, 217) PbO is dimorphous according to Ditte (C R 94, 1310)

Occurrence -As lead ochre, in small quan tities in Mexico, Baden, Virginia, and a few other localities

Formation -1 By heating Pb to low red ness in presence of air, if the temperature is kept below the melting point of the PbO, the oxide is obtained as a yellowish powder, known com mercially as massicot, if the PbO is melted during the preparation, the oxide solidines to a scaly reddish solid known as htharge -2 By heating Pb with KNO, -3 By strongly heating red lead in air -4 By strongly reating white lead on an iron plate -5 By adding boiling Pb acetate solution to boiling KOHAq, pp 18 crystalline (Winkelblech, A 21, 21, J pr 10, 227) -6 By slowly pouring Pb acetate solu tion into CaOAq at 80° until a crystalline crust appears, then adding a little more, and allowing to cool (Brendecke, R P 55, 318) -7 By add ing PbSO,, made into a paste with water, to boiling NaOHAq (Wichmann, C C 1860 334) For modifications of these processes v Payen, J pr 13, 485, Behrens, B J 24, 134 8 Ac cording to Yorke (P M [3] 5, 82), crystals of PbO are produced by placing Pb in a vessel of water exposed to the air The reaction of steam with Pb at white heat produces PbO

Preparation -1 Basic Pb nitrate is heated in a Pt crucible until comp etely decomposed (the neutral salt melts before decomposition is Berzelius recommends the following complete) procedure Equal we shts of PbO and Pb2NO, are kept in boiling water until the PbO is wholly transformed into basic nitrate, the basic salt is dissolved in boiling water, the solution is filtered hot and allowed to cool, the basic nitrate which separates is subjected to the action of the boiling solution as long as any solid separates on cooling.

A small quantity of the basic nitrate is made into a paste with water, the inside of a Pt crucible is covered with this paste, and the crucible is dried, the rest of the salt is strongly pressed while moist, then dried, and broken into smaller pieces, which are placed in the crucible, which is then heated until the decomposition is completed PbO formed from the pieces of basic nitrate in the middle of the crucible is pure, the outer layers of PbO contain a little Pt —2 PbO is prepared in crystalline form by dissolving PbO, prepared as in 1, in hot KOHAq or NaOHAq and allowing to cool The colour and S G of the crystals vary with the conditions (C R 94, 1310) obtained a greenish crystalline mass (8 G 9 1699) by heating KOHAq c 13 p c with PbO xH₂O, using 25 p c KOHAq he obtained sulphur yellow lustrous crystals (8 G 9 2089), brownish needles (8 G 9 8835) were obtained by using 30 pc KOHAq and allowing to cool, KOHAq 185 pc, saturated with PbOxHO when hot, gave deep green, almost black, crystals on cooling (SG 95605), satu rated KOHAq boiled with PbO xH2O gave deep rose coloured crystals of PbO (SG 9 4223), differing in form from the usual crystals, and becoming yellow when strongly heated (cf Mit scherlich, J pr 19, 451, Calvert, B J 24, 135, Becquerel, A Ch [2] 51, 105)

Properties -PbO is a yellow to reddish yellow erystalline solid, the colour and SG of the oxide when well crystallised seem to vary with the conditions of formation, v Preparation, Melts between 585° and 630° to a clear No 2 dark red liquid According to Leblanc (B J26. 193) molten PbO absorbs O, which it gives off on solidifying PbO is sl sol water, 1 part dissolves in c 7000 water, the solubility is affected by the state of aggregation of the PbO (cf Bineau, C C 1855 877), if the solution is exposed to the air CO, is absorbed, and the Pb ppd as basic carbonate, the PbO is also removed by filtration through paper (Yorke, P M [3] 5, 82) Heated to between 300° and 450° in air, PbO is oxidised to Pb₅O₄, but at higher temperatures Pb₂O₄ is deoxidised to PbO PbO is soluble in warm cone kOHAq or NaOHAq Geuther (A 219, 56) says that two varieties of PbO exist, one yellow and the other red, the yellow crystallises in rhombic, the red

Reactions -1 Heated in air Pb,O, is formed at c 300°-450°, at a somewhat higher tempera ture PbO is re formed -2 Heated in hydrogen, or carbon monoxide, reduction to Pb occurs at a little above 100°, PbO is also reduced to Pb by heating with C, Na, or KCN—3 Reacts with most acids to form salts PbX2, X = NO3, Cl, 3SO4, &c , absorbs CO, from the air forming PbCO, 4 Decomposes alkali salts with separation of the alkali -5 Dissolves in warm fairly conc potash or soda solution, probably with formation of plumbites $K_2(Na_2)PbO_2$ —6 Dissolves in mol ten potash forming K_2PbQ_2 which, on long con tinued heating in air, is oxidised to K_2PbO_3 (Carnegie, C N 60, 113) (v PLUMBATES under LEAD PEROXIDE, p 132) -7 Dissolves also by boiling with milk of lime on evaporating in ab-sence of air a compound separates in needles, probably CaPbO, -8 Molten PbO dissolves

in hexagonal, forms

Vor. III

silicates readily dissolve CaO, Al₂O₂, &c -9 Heated in chlorine, bromine, or rodine vapour, the compound PbCl₂, Pb₇Br₁₁O₂, or Pb₈I₄O₆, is formed, heated with Cl and air, Br and air, or I and air, the product is PbsCl16O, PbsBr,O2, or $Pb_{\bullet}I_{2}O_{\bullet}$ (Cross a Sigiura, C J 33,405) —10 By boiling excess of PbO with cone calcium chloride solution, filtering, and washing with alcohol the pp that forms on cooling, André (C R 104, 359) obtained 2PbO CaO CaCl₂ 4H₂O, by using strontium chloride he obtained 2PbO SrCl 5H2O 11 PbO does not react with phosphorus trichloride at 160°, but when heated together over a flame, PbO and PCl, react violently forming PbCl₂, Pb(H₂PO₃)₂, and P (Michaelis, J pr [2] 4, 449) —12 Dissolves in magnesium chloride so lution, on filtering and evaporating, the oxy chloride 3PbO PbCl, H,O separates (Voigt, Chem Zertung, 13, 695)

HYDRATES OF LEAD MONOXIDE -1 3PbO H,O, obtained by adding c 400 grams KOH to 1000 cc water containing freshly ppd PbO in suspension (Ditte, C R 94, 1310), also by adding basic Pb acetate solution to NH, Aq at 20°-25°, and digesting the pp under the liquid for some time (Payen, A Ch [4] 8, 302, Behrens, B J 24, 134) This hydrate forms lustrous octahe dral crystals, S G 7 592 at 0° (Ditte, C R 94, 1310), loses some H₂O at 130°, and is entirely dehydrated at 145°, e sol caustic alkali solu tions —2 2PbO H.O By ppg Pb(C₂H₂O₂)₂Aq by KOHAq or NaOHAq, and digesting with ex cess of pptant, if Pb(NO₃) is used some basic nitrate is always formed (Schaffner, A 51, 175) The hydrates of PbO readily absorb CO2 from the air, they also combine with NH, to form PbO H2O 2NH, and 8PbO 2NH, H2O (Calvert, C R 23, 480)

Plumbites Although PbO is a markedly basic oxide, it nevertheless dissolves in alkali solutions to form unstable salts of the form MinPbO2, these salts, plumbites, have not been much investigated, according to Carnegie (C N 60, 113) K plumbite is formed by dissolving PbO in molten KOH, and on long continued heating in air it is oxidised to plumbate K, PbO, The Ag salt is produced by adding NaOHAq to a mixture of a Pb and a Ag salt, Wöhler gives the formula Ag₂O 2PbO Krutwig (B 15, 1264) ob tained a yellow salt, Ag₂PbO₂ 2H₂O, by adding AgNO, Aq to alkaline Pb(NO,), Aq, and washing with hot KOHAq and then with hot water, the salt soon became black in the air

LEAD SI SQUIOXIDE Pb2O3 (Plumbo plumbic oxide) Mol w unknown, as oxide has not been A reddish yellow powder resembling gasined PbO, Debray describes Pb O, as greenish-brown (C. R. 86, 513) Debray (lc) prepares this oxide by heating PbO₂ to 350°, or by heating PbO or better PbCO₃ to the same temperature in a stream of air or O, Carnelley a Walker (C J 53, 85) say that PbO. is changed to Pb2O, at 280°-200°, and that Pb.O. gives off O at c 370° According to Jacquelain (J pr 53, 153) Pb.O. may be obtained by pouring a solution of red lead, Pb,O, in glacial acetic acid into very dilute NH.Aq, separating the pp quickly washing it with hot water containing a very little acetic acid, and drying at 100° Winkelblech (A 21, 21) obtained this oxide by pouring NaOHAq into silica, easily forming glass like silicates, these Pb(C₂H₃O₂),Aq until the pp dissolved, and then adding cold NaClOAq, taking care to avoid excess which would produce PbO₂ Debray asserts that this method yields only a mixture of PbO and PbO₂ Pb₂O₃ is not decomposed by heat until c 360°, but a little above this temperature it gives off O₄ leaving Pb₂O₄, heated to c 530°, PbO is produced (Carnelleya Walker, C J 53, 85) Pb₂O₂ is resolved by acids into PbO₂ and a salt of PbO, Winkelblech's statement that Pb₂O₃ is dissolved unchanged by HClAq, from which solution it may be ppd again by alkalis, is defined by Hausmann (A 91, 235) Pb₂O₃ is reduced to PbO by $H_2O_2O_4Aq$ or H CO₂HAq

HYDRATE OF LEAD SPSQUIONIDE Pb.O. 3H,O Obtained by adding PbO to cone K.PbO.Aq, as a red curdy pp (Seidel, J pr [2] 20, 200) The solution of K.PbO. so than ed by dissolving pure PbO. in molten KOH with a very little water, and then dissolving the fused mass in a small

quantity of water

RED OXIDE OF LEAD Pb,Q (Diplumboplumbic carde Red lead Minium) Mol w unknown, as oxide has not been gasified S G 9 096 at 15° (Herapath, P M 64, 321)

Occurrence — Minium is found mixed with other lead ores in Yorkshire, Anglesey, Virginia,

the Eifel, &c

Formation—By heating PbO in air to low redness (not above 450°) for some time, and cooling slowly—2 By adding PbO in KOHAq to K₂PbO₃Aq, washing the pp with hot water, and heating it—3 Finely divided ppd Pb exposed to air in presence of water and a little NH₃Aq is slowly changed to Pb₂O₄ mixed with Pb carbonate (Schonbein, J pr 74, 323)

Preparation—1 A mixture of 1 pt KClO₃,

4 pts PbO (prepared by heating PbCO₃), and 8 pts KNO₃ is heated, the mass melts, and PbO₂ is formed and on continued heating is changed to Pb₂O₄, the fused mass is treated with water and the residue is boiled with dilute KOHAq, to dissolve unchanged PbO, washed and dried (Levol, J pr 22, 38) -2 5 to 6 pts Pb(NO₃)₂ are dissolved in water, and KOH is added until the pp which forms is dissolved, to this liquid is added 1 pt PbO2 and the whole is boiled for some time, unchanged PbO2 is decomposed by digesting with H₂C₂O₄Aq, and the PbC₂O₄ formed is dis solved in KOHAq, the residue is washed and dried (Levol, lc) —3 Commercial red lead usually contains some PbO, this may be re moved by digestion with dilute acetic acid, or better with lead acetate solution Lowe (D P J 271, 472) recommends to digest 1 pt commercial red lead with 10-15 pts of a 10 pc solution of Pb(NO₃)₂, for some time at a gentle heat, then to boil, and finally wash well

Properties—A scarlet crystalline granular powder, when heated it becomes brighter red and then violet, at c 500°-530° decomposition to PbO and O occurs S G according to different observers varies from 8 94 to 91 (v Clarke's Specific Gravity Tables [2nded], p 47) Insol water, reacts with dilute acids to form salts of PbO, and PbO, which remains undissolved with cone H₂SO₄, or HClAq, gives salts of PbO and O or Cl Dissolves completely in glacial acetic acid forming a liquid which acts as an energetic oxidiser (v Reactions, No 6) Ph₂O₄ is readily reduced to PbO, e g by SO₂Aq or HNO₂Aq

Reactions -1 Heated to c 500°-530°, gives

PbO and O -2 Reduced to PbO by easily oxidised bodies, e.g. SO,Aq, HNO,Aq, solution of sugar -8 With stannous chloride gives PbCl2 and SnCl, -4 Dissolves in considerable quantity of cone cold hydrochloric acid to form u yellow liquid from which alkalis, alkaline carbonates, borates, and acetates, and oxides and carbonates of Ba, Mg, Zn, &c ppt PbO2, on heating, the solution decomposes to PbCl2 and Cl, this solution almost certainly contains PbCl, on warming Cl is evolved and PbCl, ppd (Fisher, C J 35, 282, v Lead tetrachloride, Dilute HClAy forms PbCl2, H2O, p 126) and PbO₂. Warm HClAq in excess evolves Cl and ppts PbCl₂—5 Dilute sulphuric, nitric, or acetic acid, and other dilute acids ppt PbO, and form sulphate, &c of PbO Hot cone H2SO4 forms PbSO₄ and O -6 Pb₃O₄ dissolves in glacial acetic acid, this solution is strongly oxidising, eg it converts SO_2Aq to SO_3Aq , As_2O_3Aq to As_2O_5Aq , PbS to $PbSO_4$, Pb, Hg, and Cu to oxides, separates I from KI (Schönbein, J pr 74 315), when dropped into dilute NH,Aq a pp of Pb₂O, is produced (Jacquelain, J pr 53, 153, v Lead sesquioxide, p 129) According to Jacquelain (loc cit) a solution of Pb₂O₁ in glacial acetic acid at 40° gives crystals of PbO₂(C₄H₂O₃), [O=8, C=6] [old notation], these crystals may be kept under acetic acid but give PbO₂ and H₄C₂O₂ on warming, or with water Schonbein (J pr 74, 315) says that conc acetic acid dissolves about 9 p c of Pb₃O₄ when shaken for 15 mins with excess of the finely powdered oxide, the solution is easily decomposed by heat or dilution, but is stable at c -18°, by careful addition of H₂SO₄, PbSO₄ is ppd and an acetate corresponding to PbO2 remains in solution, this solution deposits PbO2, slowly at ordinary temperatures, quickly when heated, addition of KOHAq does not ppt Pb₃O₄, but a mixture of PbO and PbO₂—7 Pb₃O₄ dissolves in conc phosphoric acid, the solution reacts similarly to that of Pb.O. in acetic acid By using a mixture of phosphoric and sulphurio acids, a solution is obtained containing only the phosphate corresponding to PbO, and free from PbO (Jacquelain, J pr 53, 152, v Lead per oxide, p 131) -8 Conc solutions of arsenic and tartaric acids dissolve Pb,O4, the solutions re semble those in acetic and phosphoric acids, but are more easily decomposed

Composition and constitution of red lead -When PbO is heated in air, O is slowly and con tinuously absorbed, when c 176° pc O has been absorbed the product is red, but absorption of O continues, and some specimens of red lead contain 2 67 pc O in excess of that contained in the PbO (Jacquelain, J pr 53, 151) An absorption by PbO of 179 pc O corresponds with the formation of Pb,O,, the formation of Pb,O requires 2 39 p c Older analyses of red lead led to the supposition that it was Pb2O8 (Dumas, B J 13, 113) Careful syntheses and analyses have, however, shown that a definite red coloured oxide exists having the composition Pb,O. At the same time the analyses of commercial red leads made by Mulder (J pr 50, 438) and Jacquelain (J pr 53, 151) show that the percentage of O above that required to form PbO varies from 116 to 267 Several samples of red lead agreed in composition with the formula Pb.O.

others approached Pb₂O₇ (c) Löwe, D'P J 271, 472) It is still doubtful whether a series of oxides exists of the form xPbO yPbO, x varying from 1 to 3 or 4 and y from 1 to 2 or 3, or whether only two such oxides are 'definite bodies, viz $PbO PbO_2 (= Pb_2O_2)$ and $2PbO PbO_2(=Pb_3O_4)$

Red lead, Pb₂O₄, may be regarded either as 2PbO PbO₂ or as PbO Pb₂O₃, the reaction of Pb,O, with acids, the synthesis of Pb,O, by the action of PbO in KOHAq on K₂PbO₃ (= K₂O PbO₂), and the fact that PbO2 is acidic towards some

oxides, point to the constitution 2PbO PbO₂ rather than PbO Pb₂O₃

LEAD PEROXIDE PbO₂ (Brown oxide of lead Pucc oxide of lead Lead dioxide) Mol w unknown, as oxide has not been gasified SG 8 902 at 16 5° (Herapath, P M 64, 321), 8 756 to 8 897 (Playfair a Joule, C S Mem 3, 84), 9 045 (Wernicke, P 141, 109)

Occurrence -As plattnerite, at Leadhills, in

hexagonal prisms

Formation -1 By boiling a Pb salt with a filtered solution of bleaching powder -2 By di gesting red lead with dilute HNO, Aq, and wash ing the residue -3 By mixing solutions of Pb acetate (4 pts) with soda crystals (3½ pts), and passing Cl into the mixture 2½ pts PbO₂ are obtained, PbCl, is not formed (Wehler, J pr 90, 383, cf Geuther, A 96, 382) -4 Вy heating PbO with KClO, to less than red heat and washing the mass with water -5 By boiling PbO rH O with K, FeCy, Aq in pre sence of KOH (2K₃FeCy₆Aq + 2KOHAq + PbO = $2K_1FeCy_6Aq + PbO_2 + H_2O$, Overbeck, Ar Ph[2] 85, 5) -6 By fusing PbO with KOH for some time (Becquerel, A Ch 51, 504) Carnegie (C N 60, 113) obtained PbO, H2O by long con tinued fusion of PbO in KOH, solution in water, and careful neutrali-ation by dilute H2SO4Aq (v. Hydrates of lead peroxide, mfra — 7 By oxidising PbO by an alkaline solution of KMnO₄ (Reynoso, C. R. 32, 646)—8 By electrolysing strongly alkaline solutions of Pb salts, the hydrate PbO, H O (q v) is deposited on the positive electrode (Becquerel, A Ch [3] 8, 405) By slowly electrolysing a solution of 1 pt Pb(NO₃), in 8 pts water, Wernicke obtained PbO, (P 141, 109) -9 PbO, is obtained, mixed with PbO, by shaking basic Pb acetate with H₂O₂Aq (Schonbein, J pr 75, 85)

Preparation -1 Very finely powdered Pb acetate is boiled with a filtered solution of bleaching powder, the liquid being poured off, and fresh solution added from time to time until no Pb is found in solution, the residue is washed with very dilute HNO, Aq, and then with hot water, and dried at a low temperature (Böttger, J pr 73, 493) -2 Fehrmann (B 15, 1882) recom mends to add a filtered solution of bleaching powder to conc PbCl2Aq at 50° to 60°, until a few drops of the supernatant liquid cease to show a brown colour when filtered, and to wash the

pp out of contact with air

Properties -A dark puce brown powder black according to Fehrmann (B 15, 1882) The native compound forms metal like, lustrous, iron-black, hexagonal crystals, S G, 9°392 to 9 448 (Breithaupt, J pr 10, 508) When heated, PbO₂ gives Pb₂O₄ and O, and at a higher temperature it is resolved into PbO and O Readily

parts with O to oxidisable bodies, eg rubbed with P or S vivid combustion occurs, sugar and gallic acid &c are ignited by trituration with PbO₂. Acids generally react with PbO₂ to form salts of PbO, cold conc HClAq seems to produce PbCl, and solutions of Pb3O4 in glacial acetic and phosphoric acids probably contain salts corresponding with PbO2 (v Re actions, No 9) PbO2 reacts with strongly basic oxides as an acidic oxide to form plumbates M¹₂PbO₂ (v infra, Plumbates) On account of its readiness to part with O, PbO, is largely used for forming a surface on which to strike 'safety' matches

Reactions -1 Heated, easily goes to Pb.O and O, and at a higher temperature to PbO and O-2 Readily gives up $\frac{1}{2}$ of its O to easily oxi dised bodies, either at the ordinary temperature or by slightly heating, eg when PbO2 is rubbed with an equal weight of H2C2O4, H2O, CO2, and PbCO₃ are formed, PbO₂ rubbed with ½ pt sugar or $\frac{1}{6}$ pt tartaric acid oxidises these rapidly, causing ignition, P is oxidised and ignited when rubbed with PbO2 (v Böttger, A 34, 94) -3 Sulphur dioxide is rapidly absorbed by PbO. with rise of temperature and production of SO. 4 Potassium wdide is decomposed with libera tion of I -5 PbO, reacts with a dilute solution of potassium ferrocyanide to form K, FeCy, pro vided the KOH produced in the reaction is neutralised by CO., with conc potassium ferricyanide solution in presence of KOH, K.FeCy, 18 formed —6 By digesting PbO₂ with ammonia solution, PbO, H₂O, and NH₄NO₃ are produced 7 Not acted on by cold nitric or sulphuric acid. with hot conc H2SO, gives PbSO, and O -8 Cold cone hydrochloric acid in excess dissolves PbO2, producing a yellow liquid which evolves Cl on heating and gives a pp of PbCl2, alkalis, alkaline carbonates, and alkaline earth oxides and carbonates ppt PbO2 from this solution, the solution almost certainly contains PbCl₄ (v Lead tetrachloride, p 126) Hot HClAq evolves Cl and forms PbCl₂—9 A basic acetate derived from PbO2 is said by Jacquelain (J pr 53, 152) to be obtained by dissolving redlead in glacial acetic acid at 40° and cooling. J gives the formula $PbO_2(C_4H_3O_3)_3$ [O=8, C=6][old notation] to the crystals which form These crystals are unchanged in acetic acid, on drying between paper, or on adding water, they are resolved into PbO, and acetic acid Similar salts derived from PbO, are obtained by dissolving red lead in very conc phosphoric and arsenic acids, but the salts are very unstable (J lc, cf Red oxide of lead, Reactions, No 6, p 130) — 10 Heated with phosphorus truchloride, PbCl₂, POCl_s, and Pb(H PO_s)₂ are formed (Michaelis, J pr [2] 4, 449) -11 Heated in chlorine, bromine, and vodine, the compounds Pb.ClO, Pb.Br.1O, and Pb.1LO, respectively, are obtained, heated in chlorine and air, bromine and air, and wodine and air, the products are Pb₁₂Cl₂₁O₄, Pb₁Br₃O, and Pb₁₁I₄O₁₀ respectively (Cross a. Sigiura, C J 33, 405) -12 PbO₂ reacts with alkalis to form compounds in which PbO, forms the negative radicle, eg the salt K2PbO. may be obtained from a solution in conc hot **EOHAq** (v infra, Plumbates)

HYDRATES OF LEAD PEROXIDE (1) PbO₂.H₂O This hydrate is formed as a brown pp, by dis

solving PbO in molten KOH, heating in air for a considerable time, dissolving the K_* PbO $_*$ produced in cold water, and exactly neutralising by dilute H_* SO $_*$ Aq (Carnegie, C N 60, 113) It is also probably obtained, at the positive electrode, by the electrolysis of strongly alkaline solutions of Pb salts (Becquerel, A Ch [3] 8, 405) By electrolysing an alkaline solution of Pb Na tartrate, Wernicke (P 141, 109) obtained a lustrous blue-black film, which had the composition PbO $_2$ H_* O, SG 6 267 (2) According to Carnelley a Walker (C J 53, 85), ppd PbO $_2$ after drying in the air for 10 days has very nearly the composition 3PbO $_2$ H_* O, at 230° this hydrate is changed to PbO $_2$

Plumbites -PbO2 reacts with acids as a basic peroxide forming salts corresponding with PbO, in some cases unstable salts derived from PbO₂ appear to be produced (v supra, Lead PbO₂ also reperoxide, Reactions 8 and 9) acts with alkalis as an acidic oxide to form salts M.PbO, known as plumbites Fremy (C R 15, 1109) obtained colourless crystals of K.PbO, 3H,O by dissolving PbO, in boiling very conc KOHAq, adding a little water, and placing over H₂SO, Seidel (J pr [2] 20, 200) obtained the salt by adding PbO₂ to molten KOH con taining a little water, dissolving the fused mass in water, and evaporating over H2SO, in vacuo The crystals form quadratic octahedra, a c =112216, they are decomposed by water with separation of PbO₂ A corresponding Na salt is known Solutions of these salts are said to yield pps of plumbites when added to solutions of various metallic salts K2PbO, is also pro duced by dissolving PbO in molten KOH and heating in air (Becquerel, A Ch 51, 504, Car negie, C N 60, 113) Crum obtained a plumbite of Ca by digesting Pb(NO₃)₂ with CaO and bleaching powder (A 55, 213) For Kassner (Ar Ph 232, 375 [1894]) For Plumbates v

Lead, oxybromides of Several oxybromides of Pb are known The compound PbO PbBr₂ is formed by heating PbBr₂ in air so long as white fumes are evolved, also by digesting PbBr₂ with solution of Pb acetate By heating PbO in Br vapour, Cross a Siguira obtained Pb₂Br₁₁O, and by heating the same oxide in a mixture of Br and air they obtained Pb₂Br₁O₂ (C J 33, 405), from PbO₂ they obtained Pb₂Br₁₁O₂ by

heating in Br

Lead, oxychlorides of PbCl₂ and PbO very readily combine when heated together to form oxychlorides from which HNO₂Aq dissolves out PbO

PbCl₂ PbO occurs native as matlockite, S G 7 21 (Greg, P M [4] 2, 120, Rammelsberg, P 75, 141), formed by heating PbCl₂ in air until fumes are no longer evolved, also by digesting freshly ppd PbCl₂ with cold Pb acetate solution (the oxychloride thus formed is (PbCl₂ PbO)₂ H₂O according to Brandes, A 10, 273), also (with H₂O) by partial ppn of PbCl₂Aq by CaOAq, thus prepared it is used as a pigment (Pattinson's white lead)

PbCl₂ 2PbO occurs native as mendipite, in yellow white trimetric prisms, SG 7 to 71, formed, according to Ditte (C R 94, 1180), by gradually adding KOHAq to PbCl₂ suspended in water, or by adding KClAq to PbO xH₂O

PbCl, 3PbO. the hydrate with 4H₂O is

formed by adding NH₄Aq to PbCl₂Aq (Berzelius); also by mixing NaCl with PbO, making into a paste with water, and allowing to stand, the product of this reaction, when washed and heated, gives a yellow powder, known as Turner's yellow, which is probably PbCl₂ 3PbO. The hydrate PbCl₂ 3PbO H₂O was obtained by Voigt (Chem Zertung, 13, 6°5) by dissolving PbO in MgCl₂Aq, filtering, and evaporating

PbCl₂ 7PbO a lustrous, golden-yellow, crystalline mass, obtained by melting together 1 pt pure NH₄Cl and 10 pts pure PbO, pouring off from a little Pb (formed by the reducing action of NH₄, set free by the PbO acting on NH₄Cl), and allowing to cool, known as Cassel yellow

By heating PbO in a mixture of Cl and air, Cross a Sigiura obtained Pb₈Cl₁₈O (C J 33, 405), by heating PbO₂ in Cl the product was Pb₈Cl₁₀O, and by heating PbO in a mixture of Cl and air the compound Pb₈Cl₁₀O, was obtained

the compound Pb₁₂Cl₂₁O₄ was obtained
According to André (A Ch [6] 3, 104)
PbCl₂ PbO, PbCl₂ 2PbO, and PbCl₂ 3PbO are ob-

tained by ppg PbCl₂ by KOHAq

Lead, oxycyanide of, v vol 11 p 341

Lead, oxylodides of Several oxylodides of lead are known PbI, PbO H₂O is formed by adding KIAq to excess of Pb acetate solution and digesting the pp in the liquid, it is a yellowish-white powder, insol water (Biandes, A 10, 269, cf Ditte, C R 92, 145) Other oxylodides, described by Kuhn (Ph C 1847 593) and Denot (J Ph 20,1) are PbI, 2PbO H₂O, PbI, 3PbO 2H₁O, and PbI, 5PbO Cross a Sigura (C J 33, 405) describe the oxylodides PbI, 1, O₁₀, Pb₂ 1₂O₄, Pb₁₁1, O₇, and Pb₉ 1₄O₈, obtained by heating PbO₂, and PbO, in I and air, and in I only

Lead, phosphide of No phosphide of Pb has been isolated with certainty Pelletier (A Ch [2] 13, 114) said that Pb takes up c 15 p c P when P is thrown on to melted Pb, or when Pb filings are strongly heated with glacial phosphoric acid, or PbCl₂ with P, but the experiments of Cloud (in Percy's laboratory) make it doubtful whether Pb and P combine According to H Rose (P 24, 326) a brown pp, consisting of a phosphide of Pb, is obtained by passing PH, into Pb acetate solution

Lead, salts of Compounds formed by repla cing the H of acids by Pb Pb forms one series of well marked salts, PbX₂, where X = Cl, NO₃, ¹/₂SO₄, ¹/₂CO₃, ¹/₂PO₄, ¹/₃AsO₄, &c PbCl₄ very probably exists in a solution of PbO₂, or Pb₃O₄, in cold cone HClAq, and $PbO(C_2H_3O_2)_2$ is said to have been isolated, these two salts belong to the series PbX, corresponding with the oxide PbO₂ Very many basic salts of Pb are known, and a considerable number of double salts The formulæ of the Pb salts are determined from analyses, comparison with the salts and com pounds of Sn, Ge, and Si, and from the vapour densities of PbCl₂ and PbMe, The following are the chief salts of lead (v CARBONATES, NI TRATES, SULPHATES, &c.) Antimonate, arsenate and ste, borate, bromate, carbonates, chlorate and ite, chromates, dithionate, hypophosphite, iodate, molybdate, nitrates and ites, pentathio nate, perchlorate, periodates, phosphates and -ite, sulphates and -ite, selenate and ite, selecates, throsulphate, trithronate, tungstates, uranate, vanadates

Lead, selenide of, PbSe Occurs native as clausthalite in the Hartz, &c, the Pb being sometimes partly replaced by Co, Cu, Hg, Ag, &c, SG 7 to 88 (H. Rose, P 2, 416, 3, 281, Stromeyer, P 2, 403, Kersten, P 46, 265) PbSe is produced by heating the constituents in the ratio Pb Se, it forms a porous, grey, soft mass (Berzelius), melted under borax small regular crystals are obtained, S G 8154 (Little, A 112, 212) Heated in air Se is vaporised, then a little PbSe, and a residue of basic selenite of Pb is left, cold HNO, Aq dissolves Pb, leav ing Se

Lead, selenocyanide of, Pb(SeCy),, v vol

ar p 348

Lead, silicofluoride of, Pb(BF₄). Long prismatic crystals, by dissolving PbO in HBF, Aq and evaporating to a syrup, partially decomposed by water or alcohol (Berzelius, P 2, 113)

Lead, sulphides of Besides PbS, which is a well marked compound, two subsulphides, Pb,S and Pb,S, probably exist, there are also indications of the formation of a persulphide

LEAD SULPHIDE (Lead monosulphide Plumb

ous sulphide) PbS

Occurrence - Native as galena, crystallised in monometric octahedra, and cubic and rhombic dodecahedra, SG 725 to 77 (v Neumann, P

Preparation -1 By mixing S with molten Pb -2 By heating PbO with excess of S 3 By the action of H,S or an alkaline sulphide on Pb salts -4 By passing CS over Pb heated a little above redness, crystals of PbS are formed (Pb thiocarbonate seems to be also produced) (Gautier a Hallopeau, C R 103, 111) —5 Well formed crystals of PbS are obtained by passing HS into a solution of c 3 grams Pb(NO₃), in 250 cc 10 pc HNO, Aq atc 15, if only c 1 pc HNO_s is present the pp is amorphous (Muck, Z [2] 4,211) -6 Crystalline PbS is produced by the action of PbO on thio urea (Reynolds, C J 45, Addition of HS to a Pb salt in pres ence of HClAq sometimes produces a red pp of 3PbS PbCl₂, on waiming and passing in more H S, PbS is formed -7 Winssinger (Bl [2] 49, 452) obtained an aqueous solution of colloidal PbS by ppg by HS a very dilute solution of a Pb salt, and dialysing, the solution was reddish brown

Properties -Lead grey crystalline solid, as prepared by fusion of Pb and S, SG 7505 (Karsten, £ 65, 394) A brown black powder, as prepared by ppn by H₂S SG 6924 at 4° (Playfair a Joule, C J 1, 137), 677 (Schneider, J pr [2] 2, 91) Melts at full red heat out of contact with air, and is said to sublime unchanged Insol in dilute acids, caustic alkalis, and alkaline sulphide solutions

Reactions —1 Heated in air evolves SO, and forms Pb and P' SO, and some PbO (Descotils, A Ch [2]55,441) —2 Heated with lead monoxide forms Pb and SO2, Pb and SO2 are also pro duced by heating with ead sulphate, if little PbS is heated with much PbSO, the chief pro ducts are PbO and SO, (v LFAD, Formation, Nos 1 and 2, p 122) -3 Melted with scrap eron FeS and Pb are formed -4 Heated in steam gives H2S, and at first PbO and afterwards Pb -5 Heated with alkaline carbonates half the Pb of

the PbS is separated -6 Boiled with dilute nitric acid Pb(NO₃)₂, S, and NO are produced. fuming nitric acid forms PbSO, and S, and sometimes Pb(NO₃)₂ - 7 Conc hydrochloric acid forms PbCl₂ and H₂S -8 Aqua regia forms PbCl, and PbSO, -9 Slowly reacts with chloring to form PbCl₂ and S₂Cl₂-10 By long fusion with potash and nitre Pb, O, is produced (Carnegie, C \bar{N} 60, 113) —11 Heated with lead, subsul phides $(q \ v)$ Pb S and Pb S are formed

Combinations - With lead chloride to form

the sulphochloride (q v) 3PbS PbCl

LEAD SUBSULPHIDES Ph.S and Ph.S Said to be formed by heating together PbS and Pb in the proper proportions (v Bredberg, P 17, 274) Pb2S is also formed, according to Berthier (A Ch 2] 22, 240), by heating PbSO, in a crucible lined with charcoal

LEAD PERSULPHIDE Addition of K pentasulphide to solution of a Pb salt gives a bloodred pp which is quickly changed, even in the liquid in which it is produced, into PbS and S Berzelius gives the formula PbS, to the per-

sulphide

Lead, sulphochloride of 3PbS PbCl₂ Obtained as a red pp by passing a little H₂S into a dilute Pb solution acidified by HCl, Renisch (J pr 13, 130) obtained the compound by passing H.S into a solution of 1 part Pb acetate in 200 parts water to which 20 parts HClAq, S G 1 168, were added Also produced as a yellowish red solid by digesting freshly ppd PbS with PbCl Aq Decomposed by H2S with formation of PbS Boiling water partly dissolves out PbCl,

Lead, sulphocyanide of Pb(SCy), v vol 11. p 350 Combines with PbBr, and PbCl₂, v. Lead bromosulphocyanide, and Lead chlorosulphocyanide, pp 125, 127

Lead, thiocarbonate of PbCS, by adding solution of an alkali thiocarbonate to a Pb salt (cf Thiocarbonates, vol 1 p 703)

M M P M

LEAD, WHITE White lead is a hydrocarbonate of Pb varying in composition, v vol 1. p 699

LEAD ORGANIC DERIVATIVES

Lead trimethyl salts Chloride PbMe,Cl Formed by the action of boiling aqueous HCl on PbMe, (Cahours A Ch [3] 62, 257, A 122, 48) Long needles resembling PbCl May be sub-May be sublimed M sol boiling water and alcohol verted into PbCl, by long boiling with HClAq

Bromide PbMe,Br More soluble than the

chloude

Iodide PbMe. I Obtained by adding iodine to PbMe, till the odour becomes permanent White mass, crystallising from water in long colourless needles which may be sublimed SI sol water, v sol alcohol On distillation with solid kOH it yields PbMe,OH, a strong basic oil smelling like oil of mustard solidifying in prisms

Lead tetra-methyl, PbMe, (110°) (B) V D 9 52 (calc 9 25) S G ° 2 034 From MeI and an alloy of lead (5 pts) and sodium (1 pt), or, better, from PbCl2 and ZnMe2 (Cahours) Colour less liquid, having a camphor like odour, insol water, sol alcohol and ether (Cahours) Accordng to Butlerow it smells like strawberries or mould It does not unite directly with chlorine or rodine, but is decomposed thereby, eg. PbMe4 + I2 = PbMe2I + MeI Acids convert it into

CH, and a salt of PbMe.

Di-plumbic hexa ethide, Pb_Et, Lead tra-ethyl SG 21471 Formed by adding sodium (1 pt) to molten lead (3 pts) and mixing the cooled and powdered alloy with EtI in flasks provided with inverted condensers When the first violent action has ceased the product is freed from EtI by distilling at 100°, and the residue extracted with ether (Klippel, J pr 81, 287, cf Löwig, J pr 60, 304, A 88, 318),
Properties — Yellowish mobile oil, insol

water, v sol alcohol and ether Decomposed on distillation By exposure to light, or by prolonged boiling with water, it decomposes with separation of metallic lead When exposed to the air in ethereal solution it absorbs O and CO2 with formation of (PbEt₃)₂O and (PbEt₃)₂CO₃ It

combines with iodine forming PbEt,I

Lead triethyl salts Chloride PbEt,Cl Obtained by adding BaCl, to a solution of (PbEt,),SO, in alcohol, or by treating (PbEt,),O, (PbEt_s)₂CO₃, or PbEt₄ with HCl Beautiful long needles, giving off a pungent odour when heated, presently decomposing with separation of PbCl2 and metallic lead —PbEt₃HgCl₃ white nacreous scales (from hot alcohol) — (PbEt₃Cl)₂PtCl₄ copper-red crystals, sl sol water, m sol alcohol and ether

Bromide PbEt, Br Long needles (from ether)

Iodide PbEt₃I From Pb₂Et₆ and 10dine, or from (PbEt₃)₂SO₄ and KI Sol ether and very unstable, the ethereal solution quickly depositing PbI₂

Cyanide PbEt,Cy From PbEt,Cl and KCy in alcoholic solution at 100° Prisms (from

Hydroxide PbEt_s(OH) From the chloride by treatment with moist Ag₂O or by distillation with KOH Needles, sl sol water, v sol alco hol and ether Has strong alkaline reaction and caustic taste Saponifies fats, ppts ferric, cupric, and argentic oxides from their salts Ppts alumina and zinc oxide, the pp dissolving in excess of the precipitant Expels NH, from its salts
Absorbs atmospheric CO₂ Fumes with HCl
When heated it gives off white vapours which powerfully excite sneezing

Carbonate (PbEt₃)2ČO2 Small hard crys tals, nearly insol water, sl sol alcohol and

ether Has a burning taste

Nitrate PbEt, NO, unctuous crystalline mass, decomposed by heat with slight detona-tion V sol alcohol and ether — (PbEt_s)₂SO₄ from the oxide and H₂SO. White crystalline pp, nearly insol water, alcohol, and ether, v White crystalline sol alcohol mixed with H2SO, or HCl, from which solution it separates in octahedra

Phosphate (PbEt₃)₃PO₄ stellate groups of crystals, v sol water, alcohol, and ether Sulphocyanide PbEt₃SCy crystals, sol

water, alcohol, and ether

PbEt,CHO2, formate PET, C, H, O, but yrate PbEt, C, H, O, oxalate (PbEt, D, C, Oxalate (PbEt, D, C, Oxalate (PbEt, D, C, Oxalate at 100°), and henzoate are crystalline

Lead tetrethide, PbEt, Mol w 328 (c 200°), (152° at 190 mm) (B) SG 162° at 190 mm) (C) SG 164° at 190 mm (C) SG 164° at 190 mm) (C) SG 166° at 190° at 190

Preparation -PbCl2 is added to ZnEt2 as long as reaction occurs The PbEt, is distilled

with steam $2ZnEt_2 + 2PbCl_2 = 2ZnCl_2 + 2PbEt_2$ and then $2PbEt_2 - Pb + PbEt_4$ (Buckton, P_M [4] 18, 212, 17, 282, A 109, 218, 112, 220, Frankland a Lawrance, C J 35, 244)

Properties -Oil, not decomposed by water or by gaseous NH_3 , CO_3 , CO_3 , CO_4 , NO_5 , O_5 , or H_2S Partially decomposes at 200°

Reactions -1 Gaseous SO, reacts forming diethyl sulphone and lead ethyl sulphinate PbEt₄+3SO₂=Et₅SO₂+(EtSO₁)Pb — 2 Iodine forms PbEt₅I and EtI — 3 Cone HCl forms PbEt_sCl and ethane

heas-isc_mylide, $Pb_2(C_5H_{11})_6$ D1-plumbic Prepared like the corresponding Pb, Et, using isoamyl iodide (Klippel) Oil, with irritating vapour Detonates with HNO,

Lead tri-isoamyl salts Chloride

Pb(C₅H₁₁)₂Cl from the oxide and HCl White needles

Iodide Pb(C,H11)2I from Pb₂(C₃H₁₁), in

ether by adding lodine [100°] Needles, insol water —Pb(C₃H₁₁)₃HgI₃ golden lamine, insol water, sl sol alcohol and ether —Hydroxide Pb(C_tH₁₁)_sOH, viscid mass, insol water, sol alcohol and ether Feebly alkaline, ppts ferric, but not cupric and silver salts

Lead tetra-phenyl Pb(C₆H₅), [225'] SG 20 1 530 Prepared by boiling 500 g of an 8 p c alloy of sod um and lead with 500 g of bromo benzene and 20 cc of acetic ether for sixty hours (Polis, B 20, 716, 3331 Small needles or dimetric prisms, ac=1 381 Decomposes at 270° V sl sol alcohol, ether, and HOAc, m sol benzene, CHCl₃ and CS₂ Heated with HClAq at 230° it yields PbCl₂, benzene, and chloro benzene

Lead diphenyl salts Chloride PbPh,Cl, Formed by passing chlorine into a solution of lead tetra phenyl in CS2, or by ppg PbPh2(NO3)2 with KCl White powder, insol alcohol and ether, v sl sol benzene

Bromide PbPh2Br2 From lead di phenyl White powder, which decom nitrate and KBr

poses before fusion

Indide Pb(C₆H₅)₂I₂ [c 103°] Formed by adding iodine to a solution of lead tetraphenyl in chloroform (Polis) Golden plates, sol chloro-

form, benzene, and alcohol

Nitrate Pb(C₆H₅)₂(NO₃)₂ 2aq Obtained by gradually adding lead tetra phenyl to boiling HNO. (SG 14) Small lustrous plates (from water) V sol hot water and alcohol Detonates when heated Boiling its aqueous solution produces a pp of the basic salt $Pb(C_6H_5)_2(NO_4)(OH)$ as a white powder which detonates when heated

Oxide Pb(C₆H₅)₂O Obtained by boiling the nitrate with aqueous NaOH (Polis, B 20) 3332) White powder, insol alcohol, ether, and

Oxy cyanide Pb(C_eH₅)₂Cy(OH) From the nitrate in aqueous solution and KCy powder, insol water, alcohol, and ether

Sulphocyanide Pb(C,H,)2(SCy)2 Formed by adding ammonium sulphocyanide to an aqueous solution of the acetate White powder, insol water and ordinary solvents

Phosphate (PbPh₂), (PO₄). Formed by adding sedium phosphate to an aqueous solu Formed by tion of the nitrate White pp, insol. usual solvents

Oxy-carbonate (PbPh2OH)2CO2. Ppd. as

a white insoluble powder by adding Na₂CO₂ to | 100° (Schunck) S (80 p.c alcohol) 7 at 15° solutions of salts of lead diphenyl

Chromate Pb(C₄H₃)₂CrO₄ From the nitrate and K₂Cr₂O₇ Yellow pp, insol water Sulphide Pb(C₄H₃)₂S From the acetate and H₂S Yellow prisms, 81 sol aloohol, v Decomposes between 80° and sol benzene 90°

Formate Pb(C6H3)2(OHO2)2 aq From lead tetra phenyl and concentrated formic acid Melts above 200°, with decomposi-Needles tion

Acetate $Pb(C_0HJ_2(C_2H_3O_2)_2$ 2aq lead tetra phenyl and glacial HOAc (Polis, B Prisms, v sol. water containing Melts at 193° when anhydrous acetic acid

Lead tetra-p-tolyl Pb(C,H,)4 [240°] 20 1433 Prepared by heating a mixture of 8 p c sodium lead alloy (300 g), p bromo toluene (120 g), toluene (40 g), and acetic ether (4 c c)for thirty hours in an oil bath Repeated crystallisation of the product from benzene and alcohol yields lead tetra tolyl and di-p tolyl (A Polis, B 21, 3424) Small needles Decomposes at 254° More sol benzene, CS₂ and CHCl₃ than lead tetra phenyl When heated with HCl at 200° it gives PbCl₂ and chloro toluene cone HNO causes decomposition with blackening, but on adding lead tetra tolyl to boiling nitric acid (SG 14) the products are lead di tolyl nitrate Pb(C,H,) (NO₃)₂ and nitro toluene Lead di-p-tolyl salts

Chloride Pb(C,H,) Cl₂. Formed by passing Cl into a solution of lead tetra tolyl in CS White powder, insol alcohol and ether, sl sol CHCl_s, benzene, and CS₂ Decomposed when Converted into the corresponding heated nitrate by AgNO_s in alcoholic solution

From Pb(C,H,), in Bromide Pb(CH,),Br2

CS₂ and bromine Resembles the chloride

Iodide Pb(CH).I. From Pb(CH), and
iodine, both dissolved in CS₂. Yellow powder,
more sol chloroform and CS₂ than the chloride or bromide

Nitrate Pb(C,H)2(NO3)2 28q Nitrate Pb(C,H)₂(NO₃)₂ 2aq Prepared as above White powder composed of very slender needles, sol water, containing HNO, sl sol alcohol Detonates when heated

Oxy nitrate Pb(C,H,)2(OH)(NO3) Formed by heating the nitrate with water, or by adding ammonia to a solution of the nitrate in dilute HNO, White amorphous powder

Chromate Pb(C,H),CrO, Insol yellow powder, ppd, by adding K2Cr2O, to a solution of

the acetate

Sulphide Pb(C,H)2S Formed by passing H.S into a solution of the acetate Transparent yellow plates (from alcohol benzene), sl sol alcohol and ether, v sol benzene, CS_2 and $CHCl_3$ Begins to turn brown at 90° and melts cHCl, at 98° It is decomposed by light

Formate Pb(C,H) (CHO₂) Formed from (C.H.), and formic acid Beautiful white Pb(O,H,), and formic acid Beautiful white needles, which at 233° blacken and decom

pose Acetate Pb(C,H,),(C,H,O2), 2aq [188 50] Formed by adding Pb(O,H,), to boiling HOAc Small white needles, more sol dilute HOAc than the corresponding phenyl compound

LECANORIC ACID C, H, O,. (a)-Orsellio acid Diorsellic acid. [158° cor] 8 04 at

(Schunck), S, (ether) 4 at 20° (Hesse), 125 at 15° (Schunck) Discovered by Schunck in 1842 and extracted from several lichens of the genera Lecanora, Variolaria, and Roccella (Schunck, 4 41, 157, 54, 261, 61, 72, Rochleder a Heldt, A 48, 1, Stenhouse, A 68, 61, 70, 218, Strecker, A 68, 108, Laurent a Gerhardt, A Ch [3] 24, 315, Robiquet, A Ch 42, 236, Hesse, A 139, 22) Obtained by exhausting the lichens with ether, dissolving the greenish white crys talline residue left on evaporation in milk of lime, ppg the filtrate with H₂SO₄, washing the pp with water, and recrystallising it from hot alcohol (Hesse) Stellate needles (containing Almost insol cold water Decomposed by heat with evolution of CO, A solution of barium lecanorate is not decomposed by CO. FeCl, colours its alcoholic solution dark purple red An ammoniacal solution of lecanoric acid forms white pps with lead subacetate and with AgNO, but the silver salt is quickly reduced, An alcoholic solution gives no pp with alcoholic solutions of lead acetate, HgCl₂, or AgNO₃, but with cupric acetate it gives an apple green pp When a solution of lecanoric acid is boiled it gives orsellic acid $C_{16}H_{14}O_7 + HO = 2C_8H_8O_4$ A solution of barium lecanorate yields, on boiling, first barium orsellate, and finally orcin C, H,O, and BaCO₃ An alcoholic solution yields, on boiling, orsellic ether An ammoniacal solution acquires, on exposure to air, a splendid purple colour, through formation of orcein Bleaching powder gives a red tint, quickly changing to brown

Salt - BaA" small stellate needles

Di-bromo-lecanoric acid C₁₆H₁₂Br₂O₂ [179°] From lecanoric acid and Br in ether (Hesse) White crystals (from alcohol), insol water FeCl, colours its alcoholic solution violet Gives off CO, on fusion

Tetra-bromo lecanorio acid C16H10Br4Ore [157°] From lecanoric acid and excess of Br in ether Pale yellow prisms (from alcohol), v sol alcohol, ether, and alkalis FeCl, colours its alcoholic solution purple Boiling barytawater decomposes it

LECITHIN C44H82O,PN (Von Lippmann, B 20, 3201), C44H90O,PNaq (Diaconoff) Protagon Occurs in the eggs and milt or soft roe of the carp and herring, the yolk of poultry eggs, the brain of man, sheep, and domestic fowl, bile of pigs, men, and oxen, retina of oxen, blood, yeast, milk, butter, radicles of sprouting lupin seeds, maize, peas, wheat, beet root, &c (Gobley, J Ph [3] 9, 1, 83, 161, 11, 409, 12, 5, 17, 401, 18, 107, 19, 406, 21, 241, 30, 241, 33, 161; Strecker, A 123, 356, Z [2] 4, 437, Kodweiss, A 59, 261, Diaconoff, Z [2] 4, 154, Liebreich, A 134, 29, Cahn, H 5, 215, Hoppe Seyler, H 2, 427, 3, 378, J 1866, 698, 744, Hermann, Z 1866, 250, Schmidt Mulheim, J Th 1883, 166, Schulze a Barbieri, J pr [2] 27, 358, H 13, 355, Heckel a Schlagdenhauffen, C R 103.

388, Copeman a Winston, J. Physiol. 10, 213, Preparation—1 Yolk of egg is extracted with alcohol ether, and an alcoholic solution of platinic chloride is added. A conspound of le orthin and platinic chloride is ppd, and this is agitated with Ag₂O, the filtrate freed from silver by HaS and evaporated (Strecker) -2 Brain is 186 LECITHIN.

exhausted with ether, and the residue extracted with absolute alcohol at 40°. The alcoholic extract is corled at 0° and filtered, and the pp of lecithin and cerebrin collected, washed with alcohol, and treated with ether. The ethereal solution of lecithin is evaporated (Diaconoff)—3. Beet root is extracted with ether alcohol, the ether evaporated and the residue dissolved in alcohol and ppd by platinic chloride. The pp is decomposed by H.S. (Lippmann)

Properties — Hygroscopic wax-like substance, which swells up in water and is v sol alcohol, ether, chloroform, and oils Boiling with baryta water produces glycero-phosphoric acid, neurine, and a fatty acid (stearic, oleic, or palmitic) According to Diaconoff lecithin from brain may be separated by dissolving in alcohol and cooling to —10°, into a stearo lecithin which separates and an oleo lecithin which remains in solution According to Strecker the decomposition by baryta may be represented thus —

 $C_{2n+8}H_{4n+18}O_{9}NP + 3H_{2}O = 2C_{n}H_{2n}O_{2} + C_{3}H_{9}PO_{4} + C_{5}H_{15}NO_{2}$ or

 $\begin{array}{c} C_{2a+8}H_{4n+14}O_0NP+3H_2O=\\ 2C_nH_{2n-2}O_2+C_3H_9PO_6+C_3H_{15}NO_2\;,\\ \textbf{thus stearo lecithin would be }C_{44}H_{90}O_9NP\;, while oleo lecithin would be $C_{44}H_{80}O_9NP$ and might be written$

(C₁₈H₃₈O₂)₂C₃H₅O PO(OH) O C₂H₄ N(CH₃), OH The particular lecithin examined by Strecker appeared, however, to be C42H84O9NP or to con tain one oleyl and one palmityl radicle in place of the two oleyls in the above formula the neurine is not present as a base appears from the observation that lecithin is hardly at tacked by dilute (10 p c) sulphuric acid (Gilson, H 12, 585) The neurine salt of distearyl glycero phosphoric acid appears therefore not to be a true lecithin (v GLYCERIN) According to Lippmann the base obtained by boiling beet root lecithin with baryta is sometimes neurine and sometimes betaine The presence of lecithin enables a solution of glucose to absorb oxygen from the air in the same way as an alkaline solution of that sugar (Nencki a Sieber, J pr [2] 26, 17)

Salts—The hydrochloride is a waxy mass—(C₄₂H₅₃O₅PN)₂PtCl₅ yellow flocculent pp v sol ether, chloroform, and benzene, but ppd from these solutions by alcohol (Strecker)—CdCl₂ gives a pp in a solution of lecithin in ether-alcohol

LEDITANNIC ACID C₁₈H₂₀O₈ Occurs in the leaves of the marsh wild rosemary (*Ledum palustre*) (Willigk, A 74, 363, Rochleder a Schwartz, A 74, 366, Z 1866, 382, Thal, J 1883, 1401) Prepared by ppg the alcoholic decoction of the leaves with water, and the filtrate with lead acetate The pp is dissolved in dilute HOAc, filtered, heated to boiling, and ppd with lead subacetate The pp is suspended in water and decomposed by H₂S, and the filtrate evaporated in a current of CÔ₂ Reddish powder, v sol water and alcohol FeCl₂ colours its aqueous solution dark green Lead acetate and SnCl₄ give yellow pps Boiling dilute H₂SO₄ forms ledixanthin but no sugar

Ledizanthin C,H_sO_s is a reddish-yellow powder, w. sol alkalis. Its alcoholic solution

gives & reddish-brown pp with lead acetate On

dry distillation it yields pyrocatechin

LEDUM OIL An oil obtained by steam distillation from the leaves of ledum palustre cording to Willigk (Sats W 9, 302) it consists of a terpene and of an oxygenated oil C₈₀H₁₂₈O₈ Grassmann (Rep Pharm 38, 53) obtained a volatile oil (1 pt) and ledum camphor (2 pts) Fronde (J pr 82, 181) found the oil to be acid and to contain a tergene (160°) and an oxygenated oil (241°) According to Trapp (Russ Zeit Pharm 1874, 289) the oil when recently prepared is yellowish, viscid, lighter than water, and possesses a pungent odour, when exposed to air the greater part solidifies to a crystalline mass soluble in alsohol The solution of this solidified oil (ledum camphor) in H.SO, is turned violet by HNO, Ivanoff (Russ Zeit Pharm 1876, 577) found ledum oil to consist of a white crystalline mass saturated with oil By repeated crystallisation from alcohol white prisms of C₅H₈O₂ were obtained These were insol water, v sol alcohol, ether, chloroform, and benzene, melted at 101°, boiled at 174°, and were dextroro-tatory in alcoholic solution According to Hjelt a Collan (B 15, 2500) ledum camphor melts at 101°, and has a vapour density 12 33 correspond ing with the formula C₂₅H₄₄O₂ (calc 13 02), and sublimes in long white needles Rizza (J R 19, 319) gives the following properties for ledum camphor, $C_{15}H_{26}O$ [101°], (292° 1 V), VD 8 10, and states that Ac_2O at 150° converts it into a sesquiterpene C₁,H₂₄ (264°), S G º 935

LEGUMIN © PROTEIDS

LEKENE C_xH_y ([9°] S G = 939 Forms the chief constituent of ozokerit or mineral wax, from which it is isolated by distilling the wax m vacuo, dissolving the distillate in benzene, and precipitating with absolute alcohol (Beilstein a Wiegand, B 16, 1547) White glistening crystals S (96 p c alcohol at 16°) = 0105, S (benzene at 15°) = 8, sparingly sol in most other cold solvents, e sol hot benzene and chloroform, insol acetone It decomposes on distillation under ordinary pressure, but can be distilled m

vacuo It is very stable towards oxidising agents
LEMON OIL Obtained by pressure from the peel of the fruit of citrus medica Contains a terpene C₁₀H₁₆ (166°) (Blanchet a Sell, A 6, 281, Soubeiran a Capitaine, A 34, 317) or (175°) (Regnault, J 1863, 70, A 52, 171) SG 85 at 15°-22° The terpene is dextrorotatory, $[a]_D$ = 109° (Kanonnikoff, Bn 3, 299) According to Wallach (A 227, 290) oil of lemen contains pinene and hesperidene (cf Deville, A 71, 348, In examining the es-Oppenheim, B 5, 628) sential oil obtained by steam distillation from lemon peel, Tilden (Ph [3] 9, 654) found the S G to be 852 at 20°, and the rotation + 59° in a column 100 mm long In this oil he found tere benthene $C_{10}H_{16}$, citrene $C_{10}H_{16}$ (constituting 70 p c of the whole), cymene (6 p c), a dextrorotatory body C10 H18O resembling terpineol (over 200°), a compound ether C₁₀H₁₇AcO decomposed by heat into HOAc and $C_{10}H_{10}$, and $C_{11}H_{11}O_{2}$ [116°] Tilden a Dick, C J 57, 32) The citrene (176°) forms a terpene hydrate when treated with HNO. Cone H₂SO₄ converts it into an inactive hydrocarbon (176°) Bouchardat a Lafont (C R 101. 383) find in essence of lemon a terpene C10H16 (178°) with a rotatory power + 105° which yields LEPIDEN.

137

a solid inactive hydrochloride Flavitzky (BI [2] 35, 171) found in a commercial sample of lemon oil ([a]_p = +60°) a levorotatory terpene (165°), S G 42 857, [a]_p = -29 8° which formed a levorotatory hydrochloride [a]_p = -25 9°, but this was possibly an adulterant. The oil from the peel of citrus bigamalia contains a terpene (178°) S G 42 852 which is strongly dextrorotatory, and forms a crystalline hydrochloride C.H.2HCI (De Luca. J. 1857, 481)

C₁₆H₁₆2HCl (De Luca, J 1857, 481) LEPARGYLIC ACID v AZELAIC ACID

LEPIDEN AND ITS DERIVATIVES Most of these complex comp unds were first described by Zinin' It is only recently that light has been thrown on their constitution

Lepiden
$$C_{28}H_{29}O$$
 = $C_{e}H_{s}C-CC_{e}H_{s}$
 $C_{e}H_{s}CCC_{e}H_{s}$

(Tetraphenylfurfuran) (Zinin, Z 1867, 313, Japp a Klingemann, B 21, 2934 n, cf Dorn, A 153, 358) Formed, along with benzil and oily matters, when benzoin is heated with 13 times its weight of cone hydrochloric acid (saturated at 8°) for 7-8 hours at 130° The product is washed with ether, which removes the oil and benzil, after which it is recrystal lised from boiling glacial acetic acid (Zinin) Also formed when bidesyl (hydro oxylepiden), or isobidesyl, is heated with cone hydrochloric acid for 2-3 hours at 130°-140° (Magnanini a Angeli, B 22, 855)

—Lamine [175°] Volatilises at 220° Insol water, sol 170 pts of boiling alcohol, 52 pts of ether at 17°, 28 pts of boiling glacial acetic acid, 8 pts of cold benzene Boiling alcoholic potash is without action on it Nitric acid or chromic acid oxidises it to 'acicular oxylepiden' C₂₈H₂₀O₂ Chlorine has the same action, but bromine converts it into dibromlepiden With phosphorus pentachloride it yields dichlor lepiden

Chlorlepiden C₂,H₁₉ClO By treating an alcoholic solution of dichlorlepiden with sodium amalgam for 24 hours (Dorn, A 153, 355)—Large needles [143°-146°], insol ether, sl sol alcohol, v sol benzene

Dichlorlepiden C₂₈H₁₈Cl₂O Cannot be obtained by passing chlorine into a boiling solution of lepiden, as under these circumstances 'acicular oxylepiden' is formed (Zinin, J R 7, 833) By heating together equal weights of lepiden and phosphorus pentachloride (Zinin, J R 5, 22)—Needles [169°], sol 20 pts boiling

glacial acetic acid, 66 pts boiling alcohol (95 p c), v sci ether

A dichlorlepiden described by Dorn (A 153, 355), and stated by him to melt at 156°, is probably identical with the foregoing

bably identical with the foregoing Isodichlorlepiden $C_{18}H_{19}Cl_2O$ Formed, to gether with hydrodichloroxylepiden, by boiling an acetic acid solution of 'acicular dichloroxylepiden' [202°] (Zinin, J R 7, 331), or of 'sparingly soluble dichloroxylepiden,' with zinculat (Zinin, J R 7, 194)—Needles [166°], sol 174 pts boiling alcohol (95 p c), 12 5 pts boiling glacial acetic acid, sol ether Oxidation converts it back into 'acicular dichloroxylepiden'

Pentachlorlepiden C₂₈H₁₆Cl₂O By heating oxylepiden with excess of a mixture of phosphorus pentachloride and oxychloride for half an hour at 200° (Dorn, A 153, 355)—Indistinct crystals [186°], v sl sol alcohol, ether, and glacial acetic acid, v sol benzene

Hexachlorlepiden $C_{2n}H_1Cl_0O$ By heating dichloroxylepiden with the foregoing mixture for 1 hour at 200° (Dorn) — Yellow amorphous substance [80°-90°], v sol alcohol, ether, and benzene

Octoblorlepiden C₂₈H₁₂Cl₂O By heating dichloroxylepiden with the foregoing mixture for 7 hours at 210° (Dorn) — Orange yellow amorphous substance [97°], v sol alcohol, ether, and benzene

Dibromlepiden C₂₄H₁₈Br₂O Prepared by heating a solution of lepiden in acetic acid with bromine (Zinin, Z 1867, 315) Formed, along with hydrodibromoxylepiden, when 'acicular dibromoxylepiden' is treated with zine and acetic acid (Zinin, J R 7, 330)—Laminæ (from acetic acid) [190°] (Zinin), [185°] (Berlin), sol 480 pts alcohol (94 pc), 44 pts boiling, and 6b pts cold, acetic acid, 50 pts ether Oxylepiden C₂₆H₂₀O₂ Zinin has prepared

Oxylepiden C₂₈H₂₀O₂ Zinin has prepared three isomeric oxylepidens, which he distinguishes as 'acicular oxylepiden,' 'tabular oxylepiden,' and 'octahedral oxylepiden'

lepiden, and 'octahedral oxylepiden'

1 'Acicular oxylepiden' (dibenzoylstilbene)
C.H. C=C C.H.

(Magnanini & Angeli, B 22, C.H. CO CO C.H.

854, cf Japp a Klingemann, C S Pr 1889,
136) By oxidising lepiden with nitric acid
(Zinin, Z 1867, 314) By treating thionessal C₂H₀S (Berlin, A 153, 131) or tolallyl sulphide C₃H₀S₂ (Doin, A 153, 352) with hydrochloric acid and potassium chlorate By digesting benzoïn with dilute sulphuric acid (Limpricht a Schwanert, B 4, 337) In order to prepare it, 1 pt of lepiden is suspended in 10 pts of boiling glacial acetic acid, and a mixture of 1 pt of acetic acid with 3 pts of nitric acid (S G 15) is added (Zinin, lc) -Yellow needles [220°], insol water, almost insol ether, sol 200 pts of boiling alcohol (94 pc) and 22 pts boiling glacial acetic acid, v sol benzene When heated to 340° it is converted into 'tabular oxylepiden' along with a little 'octahedral oxylepiden' Chromic anhydride in acetic acid solution oxidises it to dioxylepiden C ₈H₂₀O₅. Zinc and acetic acid reduce it to lepiden. Heating with hydriodic acid has the same effect (Dorn), also distillation with zinc dust (Berlin) to mation of lepiden by reduction, the oxylepiden is probably first converted into hydro oxylepiden, which then parts with water, yielding lepiden

¹ Zinin's work appeared for the most part in the Journal of the Russian Chemical Society. The author of the present article is indebted, for his secount of this portion of the subject, to Belistein's Handbuch der organ techen Chemic.

188 LEPIDEN

(v supra). Sodium amalgam, acting on the acetic acid solution, reduces it to hydro oxylepiden $C_{23}H_{22}O_2$ (Zinin) When heated with benzoin it is reduced to lepiden, whilst the benzoin yields benzil (Limpricht a Schwanert, B 4,388) Alcoholic ammonia at 200° converts it into a mixture of two imides of the formula $C_{23}H_{21}NO$ —one derived from 'acicular,' the other from 'abiliar,' oxylepiden—whilst with methylamine it yields a methylimide $C_{23}H_{23}NO$ [161°] (Klingemann a Laycock, private communication) Heating with phosphorus pentachloride converts it into dichlorlepiden

2 'Tabular oxylepiden' (tetraphenylcroto-(C₆H₅)₂ C-C C₆H₅ (Japp a Klingemann, CO C C₆H₅

O S Pr 1889, 137) By heating acicular oxylepiden' to 340° and recrystallising the product, first from ether and afterwards from alcohol Tabu lar crystals are deposited first, then microscopic octahedra of the third modification (Zinin, J R Tabular crystals [136°], insol water, sol **5**, 16) 145 pts boiling alcohol (95 pc), and in its own weight of boiling glacial acetic acid Dissolves readily in hot alcoholic potash solution (distinction from 'octahedral oxylepiden'), forming a salt of oxylepidenic acid $C_{28}H_{22}O_{3}$ (infra) Zinc and acetic acid are without action on it, but sodium and boiling amyl alcohol reduce it to tetra phenylbutyrolactone C28H22O2 Alcoholic am monia at 200° converts it into an imide C₂₈H₂₁NO, with alcoholic methylamine at 150° it yields the methylamide of oxylepidenic acid C28H21O2(NHCH.) When heated with phosphorus pentachloride at 200° it forms chloroxylepiden C₂₈H₁₉ClO₂

3 'Octahedral oxylepiden' Only 2 pc of this compound is formed when 'acicular oxylepiden' is heated to 340° Most readily ob tained by boiling 'acicular oxylepiden' with an alcoholic solution of caustic potash or caustic Four parts of 'acicular oxylepiden' are boiled for 12-15 hours with 60 parts of alcohol (95 p c) and 3 parts of caustic soda, employing a reflux condenser The product is washed successively with alcohol, water, and ether, and is finally recrystallised from boiling acetic acid (Zinin, J R 7, 186, J 1875, 409) —Yellowish, microscopic octahedra [232°] Sol 76 parts boiling glacial acetic acid, almost insol alcohol When heated to incipient boiling it is totally converted into 'tabular oxylepiden' Boiling the acetic acid solution with zinc reduces it to hydro oxylepiden, part of which loses water, yielding lepiden A solution of chromic anhydride in acetic acid oxidises it to isodioxylepiden C28H20O3 Alcoholic potash is without action on it

As regards the constitution of 'octahedral oxylepiden,' it is probable that this compound is a stereometric isomeride of 'acicular oxylepiden,' the latter representing the maleoid, the former the fumaroid form of dibenzoyl stilbene

C₂H₃ CO C C₄H₃
C₄H₃ CO C C₄H₃
C₄H₃ CO C C₄H₃
C₄H₃ C CO C₄H₃
(*Actoular oxylepiden' [232°]
(*Maleold dibensoylstilbene)
(*Fumaroid dibensoylstilbene)

(Japp a Klingemann, C S Pr 1889, 188) Both yield on reduction the same hydro oxylepiden (bidesyl)

C,H, CO CH C,H,

C,H, CO CH C,H,

which may be converted by dehydration into lepiden

The three oxylepidens yield by destructive distillation the same so called *usolepiden* C_2 , $H_{20}O$ (*unfra*)

'tabular oxylepiden $C_{2n}H_{10}ClO_2$. By heating 'tabular oxylepiden' with a mixture of phosphorus pentachloride (1 part) and phosphorus trichloride ($\frac{1}{5}$ part) at $180^{\circ}-200^{\circ}$ (Zinin, J R 5, 21—Crystals [185°], sol 22 8 parts boiling glacial acetic acid

Dichloroxylepiden $C_{28}H_{18}Cl_2O_2$ 'Acicular dichloroxylepiden' is obtained by hea ing lepiden with four times its weight of phosphorus pentachloride and treating the product with water (Zinin, J R 5, 23) By the oxidation of dichlor-lepiden [169°] (Zinin, J R 7, 332, J 1876, 426) — Needles [202°], sol 146 parts cold, 13 7 parts boiling acetic acid, 90 parts boiling ether When boiled with zine and acetic acid it yields a mixture of hydrodichloroxylepiden and isodichlor-lepiden [166°]

When 'he foregoing 'acicular dichloroxylepiden' is heated to near its boiling point it is converted into a mixture of two new isomeric dichloroxylepidens, which may be separated by the difference in their solubility in ether 'Readily soluble dichloroxylepiden,' which forms the chief product, is very soluble in alcohol, ether, and acetic acid, and is deposited from these solutions as a soft resin Alcoholic caustic potash converts it into a salt of dichloroxylepidenic acid C23H22Cl2O3 The other isomeride, 'sparingly soluble dichloroxylepiden,' is best prepared by boiling 4 parts of 'acicular di-chloroxylepiden' with three parts of caustic soda and 40 parts of alcohol for from 20 to 24 hours It forms a granular powder consisting of microscopic prisms [230°], almost insol alco-hol and ether, sol 36 parts boiling glacial acetic acid Boiling with acetic acid and zinc converts it into isodichlorlepiden [166°] (Zinin, J R 7, 191)

These three compounds, as their mode of formation and reactions denote, are to be regarded as dichlor substitution products of 'accoular,' 'tabular,' and 'octahedral' oxylepiden respectively

A fourth dichloroxylepiden has been obtained by Dorn (A 153, 353) by treating dichlorthionessal $C_{22}H_{16}Cl_{12}S$ with hydrochloric acid and potassium chlorate —Small needles [178°], readily sol alcohol, benzene, and glacial acetic acid Not attacked by alcoholic potash at 150° Zinc and acetic acid convert it into a dichlorlepiden and acetic acid convert it into a dichlorlepiden (156°) (v supra), whilst with hydrodic acid at 100° it yields dichlorlepiden, lepiden, and oxylepiden (?)

Dibromoxylepiden $C_{22}H_{12}Br_2O_2$. Three dibromoxylepidens, concesponding with the first three of the foregoing dichloroxylepidens, have also been described by Zinin (J. R. 7, 329, J. 1876, 425) In their modes of preparation, properties, and reactions, they resemble the chloring compounds 'Acicular dibromoxylepiden' is obtained either by brominating 'acicular oxylepi-

den' or by oxidising dibromlepiden in acetic acid | solution with nitric soid Needles [222°], sol 40 parts boiling acetic acid Heated above its melting point it yields two isomeric dibromoxylepidens-'readily soluble dibromoxylepiden,' which is resinous, v sol alcohol, ether, and acetic acid, and is converted by alcoholic caustic potash into a salt of dibromoxylepidenic acid C₂₈H₂₈Br₂O₄, and 'sparingly soluble dibromoxy-lepiden' This latter is more easily obtained by boiling the acicular modification with a quantity of alcoholic potash insufficient to dissolve it Crystallises from alcohol in lemon yellow rhombic tables [239°], almost insol ether, sol 66 parts boiling acetic acid and 1,000 parts boiling alcohol (95 pc) Heated above its melting point it is converted into 'readily soluble dibromoxy-lepiden (Zinin, J R 7, 329, J 1876, 425)

Both'sacicular' and 'sparingly soluble' dibromoxylepiden, when reduced with zinc and acetic acid, yield the same hydrodibromoxylepiden (dibrombidesyl), part of which undergoes dehydration, forming dibromlepiden [190°]

Hydro oxylepiden (Bidesyl) C.H. CH-CH C.H. (Magnanini a $C_{20}H_{22}O_2 =$

C_eH, CO CO C_eH, Angeli, B 22, 853) Formed, along with lepiden, by the action of zinc and acetic acid on octa hedral oxylepiden,' or of sodium amalgam on 'acicular oxylepiden'. The product of the reac tion is ppd with water and treated with ether, which dissolves only the lepiden (Zinin, J R 7, 188, J 1875, 409) By the action of desyl bromide, C.H. CHBr CO C.H., on sodium deoxy benzoin, or of iodine on sodium deoxybenzoin

C₆H₅ CHNa C'H' CH - CH C'H' C.H. CO CH, CO COCH, (Knovenagel, B 21, 1358) -Long flat needles (from acetic acid), [251°] (Zinin), [254°-255°] (Knovenagel, also Magnaninia Angeli) Almost insol cold alcohol and ether, sol 112 pts boiling acetic acid, sol hot benzene Heated with hydrochloric acid at 130°-140° it parts with water, yielding lepiden (Magnanini a Angeli, B 22,

Tetraphenylbutyrolactone

aphenylbutyrolactone
$$(C_{e}H_{s})_{c}C-CH C_{e}H_{s}$$

$$C_{2e}H_{2d}O_{s} = \begin{array}{c|c} (C_{e}H_{s})_{c}C-CH C_{e}H_{s} \\ COCH C_{e}H_{s} \end{array}$$

By treating & solution of 'tabular oxylepidene' (tetraphenylcrotolactone) in boiling amyl alcohol with sodium (Klingemann a Laycock, private communication) — Microscopic, white [221°], sol boiling, sl sol cold, alcohol

Hydrodichloroxylepiden C. H. Cl.O. Formed, along with dichlorlepiden, when sparingly soluble dichloroxylepiden is boiled for a long time with zinc and acetic acid, or, more readily, by boiling an alcoholic solution of 'acicular dichloroxylepiden ' with sodium amalgam, keeping the liquid acid with acetic soid (Zinin, J R 7, 195, J 1875, 413) —Flat needles (from acetic acid) [261°], insol alcohol and ether, sol 205 pts boiling acetic soid

Hydrodibromoxylepiden C,H,Br,O, the action of zine and acetic acid on 'acicular' or 'sparingly soluble' dibromoxylepiden (Zinin,

J~R~7,330 , J~1876,425) — Slender needles, v sl sol alcohol and ether, sol 172 pts boiling acetic acid

Dioxylepiden C₂₈H₂₀O₈ By warming 25 pts of 'acicular oxylepiden,' suspended in 20 pts of acetic acid, with a solution of 12-15 pts of chromic anhydride dissolved in 150 pts of acetic acid (Zinin, Z 1871, 483)—Rhombic tables [157°], sol 24 pts boiling alcohol (95°) Re ducing agents are without action on it By further action of chromic anhydride it yields benzil and benzoic acid Alcoholic potash hydro-

lyses it into deoxybenzoin and benzoic acid $C_{2n}H_{2n}O_1+2KHO=C_1H_{1n}O+2C_0H_1CO_2K$ Isodioxylepiden $C_{2n}H_{2n}O_3$ By boiling 'octa hedral oxylepiden' with a solution of chromic anhydride in acetic acid (Zinin, J R 7, 190, J 1875, 410) —Laminæ [164°], sol 10 pts boiling alcohol, less sol ether, sol 4 pts boiling acetic acid Boiling alcoholic potash is without action on it (distinction from foregoing isomeride)

Oxylepidenimide C28H21NO By heating 'acicular oxylepiden' with alcoholic ammonia for 5 hours at 200°, it yields a mixture of oxylepidenimide and the isomeric tetraphenyl pyrrholone. The oxylepidenimide is separated by means of its greater solubility in alcohol (Klingemann a Laycock, private communication) —Yellow prisms (from benzene) [180°-182°] Heated to 310° it changes into tetraphenylpyrrholone (v infra)

Oxylepiden methylimide C, H, O(N CH, By heating 'acicular oxylepiden' with an alcoholic solution of methylamine for 2 hours at 200° (K. a L)—Small pale yellow plates [161°] from alcohol, well shaped crystals from carbon bi-V sol benzene, readily sol carbon sulphide bisulphide, moderately sol boiling alcohol

Oxylepidenic acid (Benzoyl triphenyl pro (C,H,),C——CH C,H, pionic acid) C24H2O2= COOH CO C.H.

(Japp a Klingemann, C S Pr 1889, 138) The potassium salt is formed when 'tabular oxylepiden' is dissolved in hot alcoholic potash (Zinin, J R 5, 18)—The acid crystallises in laminæ, v sol ether, sol 35 pts boiling alcohol (95 pc), insol water Melts at 196°, breaking up into 'tabular oxylepiden' and water

The so called usoxylepidenic acid described by Zinin (J 1877, 397) is identical with the foregoing (Japp a Klingemann, C S Pr 1889,

Tetraphenylpyrrholone
$$(C_0H_a)_2C-C\ C_aH_a$$

$$C_{26}H_{31}NO = | | | | Formed, along$$

$$CO\ C\ C_aH_a$$

$$NH$$

with the isomeric oxylepidenimide, when acicular oxylepiden is heated with alcoholic ammonia at 200° By heating oxylepidenimide to 810° As sole product when 'tabular oxylepiden' 18 Reated with alcoholic ammonia at 200° (Klingemann a. Laycock) -Small pale yellow plates [208°], sparingly sol alcohol.

140 LEPIDEN

when 'tabular oxylepiden' is heated with an alcoholic solution of methylamine at 150° $C_{28}H_{29}O_2 + NH_2CH_3 = C_{28}H_{28}NO_2$ (Klingemann a Laycock) — Yellowish lamins [267°] from acetic acid, short needles from alcohol Sl sol boiling alcohol, more sol boiling acetic acid Decomposed by distillation in vacuo into methyleteraphenylpyrrholone (prismatic crystals [158°] from benzene) and water

CO C C₆H₃
N CH₃

formed appears to be isomeric, not identical, with oxylepiden-methylimide (K a L)

Dichloroxylepidenic acid $C_{28}H_{20}Cl_2O_3$ By dissolving 'readily soluble dichloroxylepiden' in boiling alcoholic potash (Zinin, JR, 7, 191, J 1875, 411)—Rhombic laminæ [182°], from acetic acid Sol 16 pts boiling acetic acid Heated to 200° it parts with 1 mol water, and is reconverted into 'readily soluble dichloroxylepiden'

Dibromoxylepidenic acid C₂₈H₂₆Br₄O₃ By dissolving 'readily soluble dibromoxylepiden' in boiling alcoholic potash (Zinin, J R 7, 330, J 1876, 425)—Six sided laminæ from acetic acid

J 1876, 425) — Six sided lamins from acetic acid So called isolepiden and its derivatives— Under the name of isolepiden, Zinin (J R 5, 20) has described a compound which he obtained by the destructive distillation of oxylepiden, and which he regarded as isomeric with lepiden Japp a Klingemann have, however, shown (C S Pr 1889, 139) that this compound has the formula $C_{p_1}H_{p_2}O_p_1$, instead of $C_{p_2}H_{p_2}O_p_2$, and that it is formed from oxylepiden with elimina ton of carbonic oxide according to the equation

 $C_{2}H_{20}O_{2}=C_{27}H_{20}O+CO$ The name 'isolepiden' is consequently inappropriate, but will be retained here, as the constitution of the compound is unknown, and a systematic name cannot be given The formulæ of the various hydro 'isolepidens' and oxy 'isolepidens' described by Zinin must also be written with 27 instead of with 28 atoms of carbon, although these compounds have not yet

been re investigated

Isolepiden $\hat{C}_{21}H_{20}O$ (Japp a Klingemann, lc) By the destructive distillation of oxylepiden (Zinin, J R 5, 20, cf preceding paragraph) The three oxylepidens all yield this compound on distillation, but in reality it is only 'tabular oxylepiden' which yields it, as the other two oxylepidens are previously transformed into 'tabular oxylepiden' at the temperature of the reaction The distillate is washed with ether and then recrystallised, first from alcoholic potash, afterwards from alcohol The ether extracts a little 'tabular oxylepiden,' which is carried over undecomposed (Japp a Klingemann, C. S Pr 1889, 139)—Isolepiden forms yellow tabular crystals [150°] Decomposes on redistillation Sol 18 pts boiling alcohol (95 pc), and in 2 pts boiling acetic acid (Zinin, J 1877,

394) Not attacked by alcoholic potash. It is reduced by zinc dust and acetic acid to dihydro isolepiden C_2 , $H_{22}O$, and by sodium amalgam to tetrahydro isolepiden $C_{21}H_{24}O$ Oxidising agents convert it into oxy isolepiden, and ultimately into a mixture of benzophenone and benzil

Dihydro-isolepiden $C_{2}, H_{22}O$ By reducing a solution of isolepiden in from 5 to 6 pts of acetic acid with zinc dust The product is poured into water, and the pp is washed with ether and recrystallised from alcohol (Zinin, J 1877, 394)—Small rectangular prisms [182°] Sol 12 5 pts boiling alcehol (95 p c), v sl solather

Tetrahydro isolepiden $C_{27}H_{24}O$ By the action of sodium amalgam on a boiling alcoholic solution of isolepiden (Zimin) Separates from ether as a soft resinous mass which noon becomes crystalline [132°] Readily so alcohol and acetic acid, less sol ether dride oxidises it in acetic acid solution, even in the cold, to dihydro isolepiden

Oxysolepiden C, H $_{0}$ O $_{1}$ Three pts of isolepiden are dissolved in 40 pts of acetic acid, and oxidised with a solution of 3 pts of chromic anhydride in 30 pts of acetic acid (Zinin J 1877, 395) —Short slender needles [161°] Sol 40 pts boiling, and 600 pts cold alcohol, and in 4 pts boiling acetic acid Boiling alcoholic potash is without action on it Zinc and acetic acid reduce it to dihydro isolepiden Excess of chromic acid oxidises it, in acetic acid solution, to benzophenone as chief product, together with benzil and benzoic acid

Oxy isolepiden, like oxylepiden, may be converted into isomeric compounds. Thus, when it is boiled with a quantity of alcohol or alcoholic potash insufficient to dissolve it, it is transformed into cunciform oxy isolepiden [162°] When this is heated above its melting point, or when ordinary oxy isolepiden is distilled, twollar oxy-isolepiden, a third isomeride, is formed Rhombic tables [152 5°] from acetic acid. Sol 13 5 pts boiling acetic acid, 80 pts boiling alcohol.

LEPIDINE v (Py 1) MFTHYL QUINOLINE LEUCANILINE 18 described under TRI-AMIDO DI PHENYL TOLYL METHANE

Para-leucaniline is described as Tri amidotri phenyl methane

LEUCAURIN v Tri ony tri phi nyl mfthank **LEUCATROPIC ACID** $C_1, H_{2i}O_5$ [74] Occurs in belladonna (Kunz, Ar Ph [3] 23, 722) Minute satiny needles Insol col α m sol boiling water, and alcohol

LEUCENES v PROTEIDS
LEUCIC ACID Described as Oxy HEXOIC ACID.
LEUCINDIGO v INDIGO

 (A Ch [2] 18, 119) found it among the products of the action of H₂SO₄ on animal substances Mulder (J pr 16, 290) showed the two substances thus obtained were identical

Occurrence -In old cheese (Proust), in fresh calf's liver (Liebig, Chem Briefe, ed 3, 453), in diseased but not in healthy human liver (Frenchs a. Stadeler, J 1854, 675, 1856, 702, 1858, 550), in the tissue of the lungs (Cloetta, A 92, 289), in the thymoid and thyroid glands, and in the pancreas (Gorup-Besanez, A 98, 7, Radziejewsky, Z 1866, 416), in the brain of oxen (W Muller, A 103, 131), in the pancreas of oxen (Scherer, J 1859, 610), in the liver and urine in cases of typhus, smallpox, leucæmia, and poisoning by phosphorus (Salkowsky, J Th 1880, 457, Valentiner, J 1854, 675, Sotnitschewsky, H 3, 391), in the stomachs and intestines if the pupe of butterflies (Schwarzenbach, J 1857, 538), in Agaricus muscarius (Lud wig, J 1862, 516), in the juice of vetches ger minated in the dark (Gorup Besanez, B 7, 146, cf Cossa, G 5, 314), in chenopodium album in young pumpkin plants (Schulze a Barbieri, B 11, 1233), and in beet root molasses (Lippmann, B 17, 2837)

Formation —1 In the putrefaction of proteids and gelatin $(B_{CP}, A 69, 20)$ and by boiling these substances with dilute $H SO_4$, or by fusing them with potash (Hinterberger, Sitz W 9, 450, A 71, 75, Zollikofer, A 82, 174, Gossmann, A 91, 130, Leyer a Koller, A 83, 332, Schloss beiger, Z 1860, 424, Erlenmeyer a Schoffer, Z 1869, 315, Hochstetter, J pr 29, 36, Ritt hausen a Kreusler, J pr [2] 3, 307) —2 In the pancreatic digestion of gelatin (Nencki, B 7, 1593, Jeanneret, J pr [2] 15, 353) —3 By acting on a bromo hexoic acid with ammonia (Hufner, J pr [2] 1, 6, Z [2] 4, 391, 616)

Preparation -Horn shavings (2 lbs) are boiled with H₂SO₄ (5 lbs) and water (13 lbs) for 24 hours with inverted condenser The product is mixed with lime, filtered, and evaporated to a smaller bulk (12 lbs) Oxalic acid is then added to acid reaction, and the liquid filtered and eva porated till a crystalline film forms on the sur Leucine mixed with tyrosine is deposited in groups of yellowish laminæ On recrystalli sation from water tyrosine is deposited first, and the mother liquor is then decolourised by animal charcoal and evaporated The leucine is recrystallised from alcohol (Schwanert, A 102, 221, cf Hinterberger, A 71, 72 Waage, A 118, 295) Leucine maj be detected and isolated by means of its sparingly soluble copper salt (C, H, NO,), Cu, although the precipitation of this salt is hin dered by free acids and by some organic bodies (Hoffmeister, Sitz W 75, 469)

Properties—Soft nacreous scales (from alsohol) resembling cholesterin. It may be sublimed (Mulder) Decomposed on fusion, giving amylamine, CO₂, and NH. Lavorotatory (Lewkovitch, B 17, 1439, cf Mauthner, H 7, 223) SI sol water and alcohol, insol ether. Its solubility in water is increased by the presence of acetic acid or an alkaline acetate. When heated with baryta water at 160° it becomes inactive. The inactive leucine is changed to an active variety, lavorotatory when dissolved in aqueous HCl, by the action of Penicillium glaucum (Schuize a. Bosshard, B 18, 388).

Reactions -1 An alkaline solution exposed to the action of ozone yields CO₂, butyric acid, and NH₂ (Gorup-Besanez, A 125, 210)—2 Chlorine passed into water in which leucine is suspended forms CO2 and valeronitrile, as well as chloro valeronitrile (Schwanert) Chlorine passed into an alkaline solution of leucine forms oxy-hexoic acid —3 Nitrous acid converts it into a oxy hexoic (leucic) acid —4 Distillation with MnO2 and dilute H2SO4 yields CO2 and valeronitrile -5 Distillation with water and PbO. yields butyric aldehyde and NH, (Liebig, A 70, 313) —6 Aqueous KMnO, yields NH, oxalio acid, and valeric acid (Neubauer, 4, 106, 59) — Potash fusion gives NH, hydrogen, and potassium valerate (Liebig, A 57, 127) — 8 When heated with fuming HIAq at 140° it gives hexoic acid and ammonia (Hufner) -9 With KOH (2 mols) and MeI (3 mols) it forms potassium di methyl amido-hexoate methylo iodide C₅H₁₀(NMe₂I)CO₂K, which, when heated with moist Ag_2O_1 , yields methylamine, a salt $C_6H_9O_2K_1$ and potassium leuconate C₆H₁₁O₅K (Körner a. Menozzi, G 13, 353) -10 Leucine gives off more nitrogen when its solution is decomposed by NaBrO in presence of NH₃, than when the

NH, is absent (E Schulze, J pr [2] 31, 236)
Salts—HA'HCl crystals, v sol water
(Laurent a Gerhardt, A Ch [3] 24, 321, A
68, 365)—(HA'),HCl laminæ (Schwanert)—
(HA'),H.PtCl_e yellow crystalline pp—HA'HNO₃
colourless needles, v e sol water—CuA'₂ pale
blue scales S 033 in the cold, 07 at 100°
(Hoffmeister)—HgA'.aq laminæ Mercurio
nitrate gives a white flocculent pp in a solution
of leucine (R Hoffmann, A 87, 183)—PbA', aq
ppd by adding NH,Aq to an aqueous solution of
leucine and lead acetate (Strecker, A 72, 89)

Benzoyl derivative $C_sH_{12}BzNO_2$ is $C_sH_{16}(NHBz)$ CO.H From leuone and BzCl at 100° (Destrem, Bl [2] 30, 481) Granules, sol alcohol and ether In the preparation of leucine anhydride there is also formed the anhydride $(C_sH_{16}(NHBz)CO)_sO$, which is an amorphous body [85°] insol water and ether, ve sol al cohol Decomposed by boiling water into benzoic acid and the anhydride of leucine

 $\begin{array}{cccc} Phthaloxyl \ derivative \\ C_3H_{10}(CO_2H) \ NHCO \ C_4H_cO \ H & [132^o] \end{array} \ \ From \\ leucine, \ alcoholic KOH, and phthalyl chloride \\ (Reese, B 21, 277) - K_2A'' \ \ concentric \ groups \\ of \ small \ slender \ needles \end{array}$

Anhydrade (C₃H₁₂NO)₂O When the product of the action of BzCl on leucine at 100° is treated with alcohol leucine anhydride remains undissolved, while its di benzoyl derivative (v supra) passes into solution (Destrem, C R 86, 484) Leucine anhydride is a white amorphous body, insol alcohol, but becoming gelatinous when boiled therewith It is not easily converted into leucine by boiling water

LEUCINDIN SULPHONIC ACID v Indin LEUCINIMIDE C. H., NO Obtained in small quantity, together with leucine and tyrosine, by boiling proteids with dilute H. SO. (Limpricht a Hesse, A 116, 201, Erlenmeyer, A 119, 17, Thudichum, C J 23, 409) Formed also when proteids are treated with bromine water (Hlasiwatz a Hebermann, A 159, 328), and, together with benzoyl-leucine, by heating leucine with HOBz at 200° (Destrem, Bl [2] 30, 481). Mi-

nute white trimetric needles; insol cold, al sol boiling water, sol alcohol, m sol ether May be sublimed Not affected by boiling aqueous

acids or alkalis

Iso-leucinimide C.H.11NO Formed by heating a-amido isohexoic acid in a current of HCl at 225° (Köhler, A 184, 869) Minute white needles (from alcohol), may be sublimed Insol water, sol alcohol Not affected by boiling KOHAq or by acids

LEUCO-BROMO-QUINONE PHENOLIMIDE

BROMO-DI OXY DI PHENYL-AMINE

LEUCOGALLOL C18HeCl12O 2aq [104°] Formed by passing chlorine into a cold mixture of pyrogaliol (10 g) and glacial acetic acid (20 g), then adding cone HClAq (5 c c), and continuing the passage of chlorine The pp is washed with benzene, dissolved in ether, and ppd with benzene (Stenhouse a. Groves, C J 28, 1, 704) Crystalline crusts composed of small needles Gives off HCl and water on fusion, and forms tri chloro pyrogallol and a body resembling quinone (Webster, C. J. Proc. 3, 130). V sol water and alcohol, m sol ether, insol CS₂ and ligroin, sl sol boiling benzene. Leucogallol is converted by zinc dust and dilute H₂SO₄ to tri-chloro pyrogallol C₆Cl₅(OH)₅ (Hantzsch a Schniter, B 20, 2033) It reacts with hydroxylamine and with phenyl hydrazine Its constitution may possibly be

COC(OH), C(OH) OC(OH) C(OH) CCI, C(OH) C(OH) CO 001-001-----001 O(OH),OCI OCI,OCI -- OCI

LEUCOLINE C.H., N This base, occurring in coal tar, has been shown by Hofmann (A 47, 76, 53, 427), Hoogeweiff a van Dorp $(R \ T \ C \ 1, \ 1, \ 107)$, and others to be identical with quinoline

LEUCOLINIC ACID C.H.NO. [162°] tained from coal tar quinoline (leucoline) (10 g) by dissolving as neutral sulphate and treating with KMnO, (25 g) in boiling water, adding the latter solution slowly Cold solution of KMnO. (40 g) gives only pyridine carboxylic acids
(J Dewar, Pr 26, 65, 30, 168)

Properties — Needles Often syrupy It

then becomes crystalline by boiling with water for some days Sl sol cold water, sol alcohol The lead salt is insoluble The silver salt forms

slender needles

Reactions -1 Theorystalline acid forms with glycerine a substance resembling indole -2 A solution of the potassium salt at 200° gives aniline -3 Potash fusion gives salicylic acid, CO₂, NH₃, and hydrogen —4 When heated with soda-lime to a low red heat it forms aniline, NH,, and a small quantity of methyl-pyridine

LEUCOMATNES Bases occurring in living animals (Gautier, Bl [2] 48, 16, cf J Ph [5] 18, 354, 401, Bl [2] 48, 158) Λεύκωμα white of egg Obtained by extracting fresh beef (30 kilos) with tepid water (60 kilos) to which 25 g oxalic acid and 1 cc oxygenated water is added per litre At the end of 24 hours the whole is heated to boiling, filtered, and evaporated at 50° in vacuo The residue is extracted with 99 p c alcohol, filtered, evaporated m vacuo, redissolved in alcohol, filtered, and the alcoholic solution ppd with ether The precapitate may be separated by a series of crystalli

sations from ether, alcohol, and water, and by precipitation with HgCl, into the six following bases

Xantho-creatinine CaH10N4O Small sulphuryellow micaceous lamine, with greasy surface Slightly bitter in taste Gives off an odour like acetamide when heated Smells in the cold like a dissecting room When strongly heated it gives off an odour of loast beef, and carbonises, with evolution of NH, and methylamine. Neutral to litmus Its hydrochloride and platinochloride are crystallisable and soluble solution like creatinine is ppd by ZnCl2, this pp crystallises from hot water on cooling in groups of needles AgNO, gives a flocculent pp. crystallising from hot water in needles Mercurio chloride gives a yellowish-white pp, sol alco hol It is not ppd by iodine in KIAq Sodium phosphomolybdate gives a pp after a time Treatment with HgO forms a substance melting at 174°

Chruso creatinine C.H.N.O Crystals (from water) Feebly alkaline Its hydrochloride crystallises in needles, is soluble and not deli quescent The aurochloride is slightly soluble and forms crystalline grains The platinochloride is soluble Chrusocreatinine gives no pp with zinc acetate or mercuric nitrate, but it ppts alumina from alum ZnCl, gives a ciystalline powder HgCl, gives a pp I in KIAq gives a pp Sodium phosphomolybdate gives

an abundant yellow pp

Amphicreatine C,H,,N,O, Feeble base, forming bright yellow crystals Its hydro chloride is crystalline and non deliquescent. Its platinochloride is soluble and forms lozengeshaped tables It ppts sodium phosphomolyb date, but not HgCl2

Flesh coloured Pseudocreatine C.H.N.O powder composed of minute crystalline grains Forms a very soluble hydrochloride, resembling that of hypoxanthine, crystallising in whet stone like shapes Its aqueous solution is ppd by HgCl. AgNO, gives a gelatinous pp Ppd by ammoniacal but not by neutral lead acetate When evaporated with HNO, like xanthine it leaves a residue which is turned orange red by

A base C11H24N10Os crystallising in colourless rectangular tables, with crystalline hydrochloride and platinochloride

A base C₁₂H₂₅N₁₁O₅ resembling both the preceding and xanthocreatinine

LEUCONIC ACID
$$C_5(OH)_{10}$$
 or C_5O_5 5aq 16
 $(HO)_2C < C(OH)_2 C(OH)_2$ or $OC < COCO$ $COCO$ $COCO$

croconic acid Deca oxy pentamethylene pared by adding finely powdered pure croconic acid (1 pt) to cooled HNO, of S G 1 36 (6-8 pts); the mixture solidifies to a magma of colourless needles, which are washed with ether alcohol and finally with ether (Nietzki a Benkiser, B 19, 301, of Will, A 118, 117, Lerch, A 124, 20) Gum like mass V e sol water, sl sol alcohol, insol ether Sweet taste It is readily reduced to croconic acid By dissolving in alkalis it is entirely altered Treated with tri amido benzene it forms a violet colouring matter, turned brown by alkalis (Witt, C J 49, 402)—KC₂H₂O₂: amorphous, sl sol water —Ba_s(C₅H₅O₆), doc-culent pp —Pb₅(C₅H₅O₆), pp —Ag₃C₅H₅O₆ (W) Penta oxim C₅(NOH), Yellow orystalline

solid Formed by the action of hydroxylamine apon croconic or leuconic acid. Decomposes auddenly at 172° — C.H., N.O.K.. very explosive The penta oxim may be reduced by C(NH.) C(NH.)

SnCl, to CH(NH2) ·C(NH₂, Ċ(NH₂)

forms crystalline salts

Tetra acetyl derivative of the pentaoxem C_s(NOH)(NOAc), aq (from benzene) From the penta oxim and Ac₂O at 45° (Nietzki a Rosemann, B 22, 916) Plates (from Ac₂O) or needles containing chloroform (from chloro-form) Sl sol hot benzene Decomposed at 100°

Tetre-oxim C,H,N,O, i e

C(NOH) C(NOH) When potassium croco-·C(NOH) Ċ(NOH)

nate (30 g) is gradually added to a cooled mixture of $HNO_x(45 g)$ of SG 1 39 and water (40 g), and the product is diluted with water (500 c c) and heated with hydroxylamine hydrochloride (180 g) for some hours at 45° and finally at 100° there is formed a pp of mixed oxims This is dissolved in aqueous Na, CO, and CO, is passed in, whereupon the penta oxim is ppd while the tetra oxim can be ppd from the filtrate by HCl Yellow pp Explodes at 160° sodium derivative is v sol water, but is ppd on adding alcohol or NaCl, apparently in the form of Na₂C₃H₂N₄O₅ Carbonyl-di-toluquinoxaline C₁₈H₁₂N₄O 1.6

 C,H_{\bullet} Leuconic-acid-C N

[above 300°] di tolylene-o diamide Formed by adding a salt of tolylene-o diamine to a cold aqueous solution of leuconic acid Golden yellow needles V sol warm chloroform, sl sol hot alcohol and acetic acid, insol water

Phenyl hydraside (CH,N2),C, CN2HPh Red needles (from acetic acid), v sol chloro form, sl sol alcohol Weak base The hydrochloride forms a dark-green pp (Nietzki a Ben kiser, B 19, 776)

LEUCOTIN v COTO BARK

LEUCOTURIC ACID C.H.N.O. Oxalantın Formed when a solution of alloxanic acid is rapidly boiled down to a syrup, cold water is then added which leaves the leucoturic acid un dissolved (Schlieper, A 56, 1) Formed also by reducing parabanic acid with zinc and HClAq in the cold (Limpricht, A 111, 134) White crystalline powder, insol cold, m sol hot, water Decomposes alkaline carbonates on boiling De composed by heating with KOH, giving off NH, and forming oxaluric acid Its ammoniacal solution is ppd by AgNO₃, and on boiling reduc sion takes place Boiling conc HNO, does not attack it

LEVONIC ACID C₁₄H₁₂O₄ 3aq An acid said by Wiederhold (C C 1884, 971) to be obtained by boiling levulose with baryta water Yellowish brown powder, v sol alcohol and water composed by heat.

LICARENE C₁₆H₁₆ (168°-172°) S G 18 835 An inactive terpene obtained by the action of ZnCl, or P,O, on the essential oil of Licars Kanah (Morin, A Ch [5] 25, 427) Cone HClAq forms C₁₀H₁₀2HCl, a colourless liquid, S G 12 1 069, mactive to light, and decomposed on distillation into licarene and hydrochloric acid The essential oil C₁₀H₁₈O might be looked upon as licarene hydrate and exhibits the following properties — (198°) at 755 mm S G 12 568. [a]_D = -19 at 15° It is sol alcohol, ether, and glycerın

LICHENINE C.H,O, Occurs in Iceland

Preparation - Cetraria islandica or other similar lichen is heated for several hours with a 2 p c solution of K₂CO₄ The aqueous solution 18 ppd by alcohol (Honig a Schubert, M 8, 460, cf Knop a Schnedermann, A 55, 164, Maschke, J pr 61, 7, Davidson, N Ed P J 28, 260, Errera, Bn 1, 882, Bauer, J pr [2] 34, 49, Klason, B 19, 2541)

Properties -Gelatinous pp, v sl sol cold Boiling water forms an opalescent solution, reppd on cooling or on adding alcohol Gives no blue colour with I and H₂SO₄ Dissolves in HCl, from which solution it is ppd in snowwhite flocks by alcohol Weak hot acids convert it after some time into a dextro rotatory sugar [a]1 - +55° Glucose is also formed Two carbo hydrates, resembling soluble starch in their properties, are present in the aqueous solution

LICHENO-STEARIC ACID C14H24O4 120°] An acid occurring in Iceland moss (Schnedermann a Knop, A 55, 149), and pro bably also in the fly agaric or toadstool (Bolley, A 86, 50) Obtained by boiling Iceland moss for 15 minutes with dilute alcohol and some K CO₂, filtering, adding HClAq and 4 volumes of water The pp is boiled with alcohol of 45 p c. whence a mixture of licheno stearic and cetraric acids separates on cooling The licheno stearic acid is extracted from the mass by petroleum and recrystallised from alcohol Mass of radiating needles which soon change to delicate pearly lamine Has a rancid taste Insol water, v sol. alcohol, ether, and oils Is not attacked by AcCl On oxidation it yields CO2 and decoic acid (Hilger a Buchner, B 23, 401) The ammonium salt forms a jelly containing extremely slender needles -BaA', grevish white pp which cakes together in boiling water -PbA' flocculent pp fusing under water -AgA'

LIEBERMANN'S REACTION A blue or green colour obtained by warming phenol-with H₂SO₄ containing nitrous acid It may be used as a test for phenol or for nitrous acid Various derivatives of phenol may be used instead of phenol, while nitroso and oximido compounds usually react like nitrous acid

LIGHT For an account of the applications of optical methods of inquiry to chemical problems, v Physical methods, section Optical

LIGNIFICATION v LIGNONE

LIGNO-CERIC ACID C2, H46O or C22H4, CO H [81°] Occurs in the paraffin obtained from beech wood tar (Hell, B 13, 1709) Occurs also in the product of the saponification of earth-nut oil, (Kreiling, B 21, 880) Colourless felted needles or plates (from alcohol)

Salts -A'Na white powder -A'K white

powder, sol alcohol —A'Ag white pp [c 155°] -A'2Cu green powder, sol ho benzene -

M. 25 white powder, [117°] v sol hot benzene
Methyl ether A'Me [58°] White glustening plates Sol CS₂, CHCl₃, C₆H₆, ether, and ligroin, sl sol alcohol Distils undecomposed at a high temperature

Ethylether A'Et [55°], (310° at 20 mm,

860° at 760° mm) Glistening plates Chloride C₂₃H₄₇ COCl [48°-50°] Sol ether

LIGNONE (Lignin, Lignose Lignification) Lignification, or the process of wood formation, is one of the principal of the modifications of the cell-wall, by which it and the tissues con taining it are differentiated for fulfilling their several functions The history of a lignified cell, or rather of the substance of the cell wall, is usually stated to consist of (1) the elaboration of the primary cell wall from materials in protoplasm, and formed at its limiting film as an envelope of pure cellulose, (2) the induration of this cell-wall, is lignification, by the infiltration of substances, which when deposited are known as 'lignin,' or more vaguely as 'incrustive' substance Lignification is recognised by the morphological changes with which it is associated, as well as by the very characteristic reactions of the product (Goodale, Phys Botany, These products, although presenting a wide range of differences, corresponding with variations in structural and other characteristics of the tissues which they compose, fall naturally, and as regards their chief constituent, into a homogeneous chemical group, designated by the term lignocellulose, of which the typical features are represented in the substance of the jute fibre (vol i p 719)

It is the purpose of this article to give a brief account of more recent researches into the constitution of this typical lignocellulose, and to show the bearings of the results arrived at upon the chemistry of the woods, the most numerous and important section of the group The advantages of the jute fibre over the latter as a subject of study are that it is a simple tissue, whereas the woods are complex aggregates, that as an isolated fibred it is much more easy of penetration by reagents, and that as a product of only a few months' growth it has not undergone such secondary changes in composition as necessarily take place in the substance of a perennial stem or true wood Such characteristics mark out the jute fibre substance as a natural basis for the general solution of the chemical problem of lignification

Evidence has already been given (vol 1 loc cit) for regarding this product as chemi cally homogeneous, which view is further developed in the investigations referred to (C J 1889 199) In all reactions in which hydroxyl groups only are brought into play—hydrolysis and etherification-it behaves as an integral compound (lignocellulose), of which the formula C₁₂H₁₈O₂ is an approximate empirical expression. The limit of 'nitration' is the tetranitrate, indicating a number of OH groups in the original less by two than in the molecule of cellulose, similarly represented, to as C12H20O10 The product is of a bright gold colour, with a silky lustre In further contradistinction to

cellulose, the OH groups of the lignocellulose react with acetic anhydride at its boiling point Its reaction with chlorine has been studied quantitatively, 1 grm of the purified fibre substance takes up 54-55 c c Cl (calc at 0° and 760 mm), or approximately 16 pc by weight the quantity of Cl as HCl formed being equal to that entering the molecule The chlorinated product $n(C_{19}H_1,Cl_4C_9)$, a simple substitution-derivative of the non-ellulose constituent (which we may regard as $n(C_{19}H_{21}Cl_4O_9))$, contains mairogallol in combination with a body not yet com pletely studied, but yielding furfural on hydro lysis In addition to the molecular groupings thus indicated, the presence of methyl groups is proved by the formation of methyl chloride on heating this con pound, and of acetic acid on de structive distillation of the fibre substance, as also by dissolving it in sulphuric acid, dil iting and distilling These results afford a general view of the constitution of the 'lignin' substance, as it has been termed hitherto We may regard it as con taining closed C, chains, further characterised by the presence of ketone or quinone oxygen, and united to the furfural yielding body, which is probably related to 'wood gum' ('Holzgummı')
Tollens has, in fact, isolated xylose from the jute fibre (B 22, 1046), though in very small quantity, and we would note here the increase in the proportion of the parent substance, woodgum, with the more advanced lignification of perennial stems, as additional evidence for this view It is difficult to localise the methyl groups. but they would appear to be independent of the above, and may be regarded as existing in an acetic residue in combination For a substance of marked ketonic and aldehydic characteristics, the terms lignin and lignose are obviously un suited, and should give place, according to pre sent views, to lignone, by which, therefore, we shall designate the non cellulose component of the lignocelluloses generally

The lignone of plant cells generally in the earlier stage of growth, ie lignification, appears to be not merely similar to but identical with that of jute Proof of this has been afforded by the particular investigation of such widely dif sering structures as the stony concretions of pears -- Erdmann's glycodrupose---the fibrovas cular bundles of Musa Paradisiaca (Monocot), and the bast fibres of the Sida species (C J 1882, 108, 1883, 19, 1889, 212)

But very few of the woods have been particularly investigated in regard to the constitution of the wood substance, and for the most part only in regard to the products of hydrolysis (v vol 1 p 719) Thus Erdmann concluded from his study of coniferous wood that its chief constituent-'glycolignose'-is a chemical individual $C_{30}H_{46}O_{21}$, a species of glucoside resolved by treatment with boiling acids into 'lignose' C18H26O11 and a fermentat'e sugar (glucose). The presence of closed C₆ chains in the 'lig nose' molecule was evidenced by its yielding protocatechuic acid on fusion with alkaline hy-

A more direct conversion of the lignone into definitely - A more circut conversion of the lignone into definitely aromatic products is that which takes place spontaneously when masses of jute are exposed to moisture and heat. From specimens of fibre 'rotted under such conditions Cross and Bevan obtained an astringent substance C_mH_mO_{1m} which yielded phloroglucol and protocatechulo acid on fusion with potash (C S J 1882, 93)

LIGNONE. 145

drates It was also concluded that the wood of the widely different poplar species was similar if not identical in composition (A Suppl 5,

228)

The later researches of F Bente (D P J 217, 235), although modifying these views, chiefly in the variation in the results of hydrolysis, nevertheless in the main confirm them The general conformity of the woods to the types above described as representative is shown

(1) In the close similarity of their character istic reactions Of these we may mention (a) the colouration produced with solutions of the aro matic amines (golden yellow), and of solutions of the phenols in hydrochloric acid, most cha racteristic of which is the reaction with phloro glucol (crimson), (b) the powerfully reducing action of the wood substance upon the oxides of copper, selver, gold, and mercury-showing the presence of aldehydic groups, (c) the reactions with the halogens yielding, in the case of chlorine, substitution products of definite quinone chloride characteristics, attended by complete resolu tion into lignone (chloride) and cellulose with bromine and iodine less definite compounds, but constant under constant conditions, (d) with nitric and sulphuric acids yellow-coloured ex plosive nitrates, (e) with acetic anhydride at its boiling point and with benzoyl chloride in pre sence of alkalis, the corresponding ethereal deri vatives, (f) with solutions of the caustic alkalis at 160° - 190° , with bisulphites (of the alkaline earths) at 150°-170° and with sulphurous acid (7 p c solution) at 90°-105°, attended by complete resolution into lignone (soluble derivatives) and celillose (insoluble)

(2) In their empirical composition, which shows a remarkable uniformity throughout the group. This is illustrated in the appended table of results of analyses and determinations of calorific equivalents (Gottlieb, J. pr. 2] 28, 385)—

Wood	Åsh	\itro gen	Car bon	Hy dro- gen	Calorific equivalents per 1 gram
Oak Ash Hornbeam Beech Birch Fir Pine	 0 37 0 57 0 50 0 57 0 29 0 28 0 37		50 16 49 18 48 99 49 06 48 88 50 36 50 31	6 17 6 20 6 11 6 06 5 92	4620 4711 4728 4777 4771 5035 5085

An investigation by N Schuppe of the chemical composition of a number of woody tissues (Pharm J [8] 14, 52) led to the following conclusions (a) that the woods are uniform in their characteristics, being composed of cellulose and 'lignin' in somewhat variable proportions, (b) the cellulose when isolated (Schultze's process) having the composition $C_tH_{10}O_3$, and (c) 'lignin,' being represented by the empirical formula $C_{10}H_{10}O_3$, which is closely similar to that obtained for the 'lignone' of jute Further, G W Hawes has examined the woods of typical acrogens, e.g. lycopodium, equisetum, and aspidium, and finds that they do not differ essentially in composition from exogenous woods (Am S [8] 7, 585)

Vor III.

(3) In the products of their destructive distillation, which, when carried out under uniform conditions, gives results which are very similar for the several woods A very elaborate series of such distillations was carried out by M Senff (B 18, 60), the results being given in percentages of the wood under (1) total distillate, (2) tar, (3) crude vinegar, (4) anhydrous acid (acetic), (5) charcoal, (6) gases The following numbers represent the limits of the percentages observed (1) 40-50, (2) 3-8, (4) 2-6, (5) 20-30, (6) 17-35 The woods of all the more important species, e.g. Quercus, Populus, Betula, Fagus, and Pinus, were included in the research, and shown by the results to resemble one another very closely in composition The products may be more particularly classified as regards the light which they throw upon the molecular grouping of the parent substance into (a) members of the fatty series alcohols, ketones, aldehydes, and acids generally of low molecular weights, (b) furfural and its homologues, (c) a group of aromatic bodies, constituting 'creosote,' which may be described as a mixture of guaiacol and creosol, containing besides, methyl creosol and the dimethyl ethers of pyrogallol and its homologues in varying pro portions (Schorlemmer, 'History of Creosote,' S C I 4, 152) These divisions, it will be noted, correspond with the ascertained grouping of the complicated lignone molecule (supra), of which they afford additional confirmation It is obvious that the process of destructive distillation must be attended with complications arising from secondary reactions, but the temperatures in the case of wood are sufficiently low to reduce these to a minimum thus the yields of furfural are at a maximum when the temperature does not exceed 200° (Heill, B 10, 936), and the acetic acid is increased considerably beyond the per centages given by Senff (supra), viz from 2-6 to 5-10, by raising the temperature very gradually through 150°-300° (W Rudnew, D P J 264, 88 & 128), no doubt at the expense of the methylation of the aromatic derivatives This subject. however, except in regard to the outlines which we have sketched, belongs rather to the general theory of destructive distillation

The fundamental tissue of the woods we regard, therefore, in all cases as a lignocellulose, of which the lignone portion, while possessing the typical characteristics common to the group, is no doubt variously differentiated with the specialised characteristics of families, and indeed species and individuals

In addition to the fundamental tissue the woods contain other constituents, which from their nature are seen to be more or less adventitious. They are, in fact, generally removable by the action of solvents (in the case of resins, gum resins, balands, &c.), or by simple hydrolysis. In this group we may mention such definitely aromatic derivatives as confern and vanillin (M. Singer, M. 3, 395), the tinctorial constituents of the dye woods, also the very characteristic and important constituent of most exogenous woods known as 'wood-gum' (Holzgummi), first described by Thomsen (J. pr. [2] 19, 146), who found quantities varying from 8 p. c. to, 20 p. c. of the woods examined. This body yields on hydrolysis the C, sugar, xylose (Tollens, Uniters a. d. Agr. Chem. Lab. Gtittmen. An-

Ť.

146 LIGNONE

nalen, 254, 325), which by further resolution yields furfural Whether the wood gum is a product of resolution of the lignone molecule has not yet been disclosed, but it would appear to be probable A similar remark applies to the aromatic derivatives above mentioned

In conclusion we must briefly notice a recent contribution to the subject of the 'constitution of lignin' (Lange, Ztschr Physiol Chem 14,217) This consists in a study of the soluble products of resolution of certain woods-beech, oak, and fir-by heating with strong solutions of the alka line hydrates at 185° In addition to formic and acetic acids, traces of higher fatty acids, oxalic acid and small quantities of pyrocatechol and protocatechuic acids, there were obtained certain amorphous bodies of brown colour, which the author terms lignic acids These were resolved by treatment with alcohol into (a) soluble, (b) insoluble in this menstruum. The empirical composition of these derivatives is subjoined

Lignic Beech C 613 H 54 C 590 H 54 acids River C 609 H 54 Fir C 615 H 50 C 604 H 50 The yield of these bodies is from 12 15 pc of the weight of the wood The insoluble residues from the original alkaline digestion are described as 'celluloses,' but the description is doubtful These results have an empirical value, but throw little light on the constitution of the wood sub-

(a)

stance They afford additional evidence, how ever, of the general similarity of woods of various origin

Digested with alkalis at higher temperatures (200°-250°) than those employed in the researches detailed above, the lignocelluloses are resolved for the most part into oxalic and carbonic acids. With potassium hydrate—which appears to give the maximum yield—the following proportions of oxalic acid have been obtained, the yield being calculated on the dry woods pine, 94 7 pc, poplar, 93 2 pc, oak, 83 4 pc (W Thorn, D P J 10, 24). It is evident that the oxalic acid is derived from both lignone and cellulose, which are therefore probably similarly constituted as regards the arrangement of the C atoms.

The action of the alkalis, however, at the point at which they resolve the lignocellulose is too severe to afford any trustworthy evidence, from the study of the products, as to the constitution of the original substance. The problem can only be solved by first studying those reactions which yield definite substitution or ethe real derivatives, these are chiefly chlorination, conversion into nitrates, acetates, and benzoates, and the reaction with bisulphites (solutions) at high temperatures.

In this article we do not attempt a special description of the woods or their constituents, our endeavour is rather to generalise what is known concerning the wood substance proper, that which resists mechanical solvents alto gether, and hydrolytic agents up to a certain degree of intensity

CFC

LIGRO'N The mixture of homologues of methane obtained by collecting the portion of petroleum that boils below 100°

LIGULIN A crimson colouring matter in with ZnCl₂ it yields a terpene, v Licarene By ripe privet berries (Nicklés, J Ph [3] 85, 328), prolonged treatment with saturated HClAq and

sol water and alcohol, insol ether Does not contain nitrogen Coloured green by alkalis

LIGUSTRIN A yellow hygroscopic bitter mass extracted from leaves of the privet (Ligustrum vulgare), insol ether and alcohol, sol water and dilute alcohol Cono H₂SO₄ gives an indigo blue solution (Polex, Ar Ph [2] 17, 75)

LIGUSTRON [c 100°] (260°–280°) Occurs in privet bark (Reinson, J 1847, 787) Needles, v sol water, alcohol, and ether Tastes bitter Reduces ammoniacal AgNO.

LIME Oxide of calcium, CaO, v vol 1 p

LIME, CHLORIDE OF A name sometimes given to bleaching powder, v BLEACHING FOWDER, vol n p 17

LIME LEAF JIL The fiagrant oil obtained by distilling the leaves of Citrus Limetta with steam contains a citrene (c 176°), 1 active to light, and with refractive index for red rays 14611 at 30°, terpinol, methyl ennyl ketone, and a colophene (F Watts, C J 49, 316)

climes, OTTO OF Obtained by rasping and squeezing from the unripe peel of the fruit of Citrus limetta Contains a terpene (176°) and a soft resin, not volatile at 250° On standing the resin deposits C_{2i}H₂₅O₅ [102°] (Wright a Piesse, C J 32, 548)

LIMETTIC ACID C₁₁H₈O₆ Obtained by the action of H₂SO₄ and K₂Cr₂O₇ on the oil of lime (from Catrus Limetta) and on oil of rosemary (Vohl, N Ber Arch 74, 16) White crystalline body, may be sublimed Has no taste or smell Sl sol water, v sol alcohol—Ag,A" powder, sl sol water, blackening on exposure to light

LIMETTIN C₄H₁₄O₈ [122°] A neutral body occurring in oil of limes (Tilden, C J Proc 6, 30) Tufts of pale yellow needles (from alcohol) Not acted upon by AcCl or by phenyl hydrazine Bromine forms colourless scales of C₁₆H₁₁Br₂O₈ Boiling cone NaOHAq forms NaOAc and crystalline C₁₄H₁₁(OH)O₄

LIMONENE A terpene occurring in oil of lemon and in many other essential oils, v

LIMONIN C₂₁H_{2e}O, [275°] (Paterno a Oglialoro, G 9, 64), [245°] (Hoffmann A, Ph. [3] 14, 839) A bitter substance contained in the pips of oranges and lemons (Bernays, Buchner's Rep. [3] 21, 306, A 40, 317, Schmidt, A 51, 338) The pips are exhausted with boil nig water, alcohol is added, and the mixture is boiled with inverted condenser. After filtering, and distilling off the alcohol, linionin is left, together with a fatty substance which may be removed by CS₂ 1500 g of pips yield 80 g of limonin (P a G) Laminæ, sl sol water, ether, and NH₃Aq, v sol alcohol, HOAc, KOHAq, and baryta water. The barium salt is not de composed by CO₂ Cone H₂SO₄ forms a red liquid, from which the limonin is ppd by water.

LINALOES OIL The essence of linaloes, obtained from the wood of Licari kanali, the white cedar of Caylone, is a slightly coloured liquid with an odour like rose and lemon After distillation over CaCl₂ it consists of C₁₀H₁₆O (198°) S G ¹² 868 [a]_D = -19 at 15° It is sol alcohol, ether, and glycerin When distilled with ZnCl₂ it yields a terpene, v Licarene By prolonged treatment with saturated HClAg and

LITHIUM 147

exposure to light it yields CieHie2HOi, an optically inactive liquid with a camphor like odour, and S G 12 1069 When distilled with lime it yields licarene C₁₀H₁₆, (c. 170°), S G

18 835 (Morin, C R 92, 998, 94, 733)

LININ C 629pc H 47pc Acrystallisable substance obtained by digesting Linum catharticum with milk of lime, filtering, ppg with HCl, and extracting with ether (Pagenstecher, A 40, 322, C Schröder, N Kep Pharm 10, 11) Silky crystals, v sl sol water, v e sol alcohol and ether, m sol chloroform and HOAc The alcoholic solution is intensely bitter

LINOLEIC ACID C₁₈H₂₂O₂. Linolic acid S G ¹⁴ 92 Occurs as glyceryl ether in linseed oil, hemp oil, poppy oil, olive oil, nut oil, cotton seed oil, earth nut oil, almond oil, oil of sesame, palm oil, cacao butter, and probably in most fixed vegrtable oils (Pelouze a Boudet, A Ch [2] 59, 43, Laurent, A Ch [2] 65, 150, 298, Liebig, A 33, 113, Sacc, A 51, 214, Schuler, A 101, 252, Oudemans, J 1858, 304, Hazura a Grussner, M 9, 944, 10, 242, Benedikt a Hazura, M 10, 353) It does not occur in animal oils, so that when the acids obtained by saponifying animal oils are oxidised by KMnO4 no sativic acid will be formed, but di oxy stearic acid will be among the products, this being derived from oleic acid (B a H)

Preparation -Crude linseed oil or hemp oil is evaporated with aqueous NaOH, the sodium soap is decomposed by H SO,, and the crude acid dissolved in alcohol, neutralised with NH, and ppd by BaCl₂ The barrum salt is dissolved in ether, HCl is added, the ether decanted from ppd BaCl, evaporated, and the liberated acid dried in vacuo over H SO, (Schuler, Bauer a Hazura, M 7, 216) The acid so obtained is a mixture of oleic, linoleic, linolenic, and iso linolenic acid (Hazura) By treatment with bromine at 0° and reduction of the product C18H20Br4O2 with zinc and HCl pure linoleic acid

Properties -Faintly-yellow limpid oil Does not solidify at -18° Insol water, v sol ether, m sol alcohol When distilled under 90 mm pressure one third passes over at 290°, and the distillate contains sebacic acid C₁₀H₁₈O₅ [130°] and an oily mixture (Hazuia a Grussner, M 9,

206, of Norton a Richardson, B 20, 2735)
Reactions —1 Potash fusion gives myristic, acetic, and formic acids, with traces of azelaic acid -2 KMnO, hydrogen peroxide, and MnO, with H SO, exidise it to azelaic acid -3 KMnO, in presence of KOHAq converts it into sativic acid, some azelaic acid also being formed alkaline KMnO, oxidises crude linoleic acid from linseed oil (100 g) into sativic acid $C_{18}H_{32}(OH)_4O_2$ [173°] (6 5 g), linusic acid $C_{18}H_{20}(OH)_8O_2$ [204°] (4 5 g), isolinusic acid [175°] (15 8 g), and di oxy stearic acid $C_{18}H_{34}(OH)_2O_2$ [137°] (1 2 g) (Hazura, M 9, 180 of Dieff a Reformatsky, B 20, 1211) It appears therefore that crude linoleic acid consists of linoleic acid C₁₀H₁₀O₂ (which gives sativic acid or oxidation), linolenic acid C₁₈H₁₀O₂ (which gives linusic acid), isolino lenic acid (which gives isolinusic), and oleic acid (which gives di oxy stearic acid) The formation of sativic acid in this manner may be made use of as a test for linoleïc acid —4 Bromine at ordinary temperatures forms with crude linoleic

acid solid $\mathbf{Q}_{10}\mathbf{H}_{20}\mathbf{Br}_{0}\mathbf{O}_{2}$ [177°] Bromine at 0° forms a tetrabromide $\mathbf{C}_{10}\mathbf{H}_{22}\mathbf{Br}_{10}\mathbf{O}_{2}$ [115°] (Hazura, M 8, 147, Hazura a Friedrich, M 8, 155, 265) Of these two compounds the former is formed from linolenic, the latter from linoleic acid Pure linoleic acid gives only C₁₈H₃₂Br₄O₂ [115°] — 5 Fuming HIAq and amorphous phosphorus converts it into stearic acid (Peters, M 7, 552)

Salts -The salts are not crystalline With the exception of the salts of the alkalis they are insol water They are sol ether With the ex-

ception of the Pb, Mn, Na, and NH, salts they are insol alcohol—BaA'₂(Peters)

Linolenic acid C₁₈H₁₀O₂ Obtained by treat ing the compound $C_{18}H_{30}Br_{6}O_{2}$ [177°] (v supra) dissolved in alcohol with zinc and HCl (Hazura, M 8, 267) Yields on oxidation by alkaline KMnO, no solid acid except linusic (hexa oxystearic) acid [201°] Bromine forms only Linolenic acid 'dries C₁₈H₃₀Br₆O₂ [177°] rapidly when exposed to air, through oxidation Its salts behave in like manner The more glyceryl linolenate there is in an oil the more rapidly does it dry Glyceryl linolenate and isolinolenate also possess drying properties, but glyceryl oleate does not The product produced by exposing the acids to air is an anhydride, insol ether, but furnishing soluble acids when heated with alkalis

Isolinolenic acid $C_{18}H_{30}O_2$ An acid assumed to exist in crude linoleic acid on account of the formation of isolinusic acid on its oxidation When crude linoleic acid is oxidised by KMnO. in alkaline solution, and the product ppd by H SO, there is obtained a mixture of fatty acids whence cold ether extracts dr oxy stearic acid. sativic acid remaining undissolved The filtrate from the ppd acids is neutralised with NaOH, evaporated, again ppd with H2SO4, the pp extracted with ether, and the residue crystallised from alcohol and then from water, whereby it may be separated into linusic and isolinusic acids

LINSEED OIL The oil expressed from the seeds of flax (Linum usitatissimum) Like other drying oils when exposed to the air it dries up to a transparent resinous mass Lin seed oil is composed of the glyceryl ethers of oleic, linoleic, linolenic, and isolinolenic acids v LINOLEIC ACID Linseed oil dissolves some oxide of lead when heated therewith, being decolourised and rendered more easily drying (boiled

LINUSIC ACID v HENA ONY STEARIC ACID Isolinusic acid v Hela oxy stearic acid

LIQUIDAMBAR A balsam obtained from a large tree, Liquidambar styracifolia, growing in Florida and Mexico It resembles balsam of Peru, containing cinnamyl cinnamate, styrene, and cinnamic acid (Harrison, Ar Ph [3] 6,541, Maisch, Ar. Ph [3] 6, 545)

LIQUIDS, diffusion, dispersion, osmose, refraction, transpiration, of, v Physical

LITHIUM L. At w 701 Mol w probably 701 (v p 149) [180°] (Bunsen, J 8, 324) S G 578 to 589 (Bunsen, Ic) S H 27° to 100° = 9408 (Regnault, A Ch [3]63, .1) E C at 20°, (Hg at 0° -1) 10 69 (Matthiessen P M [4] 12, 199, 13, 81) Characteristic lines in emission spectrum are Lia in the red 6705 2, and a

148 T.ITHIUM.

weaker line in the orange 6102, and a weak line in the blue 4602 7 (Thalén, 1868, v also L de Boisbaudran, Spectres Lumineux, p 55, Schönn, W 10, 143, Liveing a Dewar, T 1883 187) S V S 11 9

Occurrence - Salts of L1 are very widely distributed, but occur only in small quantities Several phosphates of Fe and Al contain Li phosphate, especially triphyline, which contains c 7 p c Li₂O, many silicates of Al and Fe con tain small quantities of Li silicate, especially lepidolite, which sometimes contains from 3 to 5 pc LiO Tourmalines, borates, &c, often sontain traces of lithia Very many mineral springs contain lithia, according to Kirchoff a Bunsen lithia is present in almost all mineral waters (P 113, 357) Truchot found lithia in the soil of Limargue in the Auvergne, nearly all the plants growing on this soil take up lithia (C R 78, 1022) Dieulafait has found traces of Li in sea water from all parts of the globe, in the water of marshes, in mineral springs, in primary rocks, in gypsum of different formations (A Ch [5] 17, 377) Lithia is found in many plants, and in all sorts of tobacco, but not in raw sugar, cocoa, coffee, or tea (Focke, Der Natur forscher, 1872 307, Grandeau, A Ch [3] 67, 216) Lithia has also been found in the milk and blood of cows (Bunsen & Kirchoff), in different parts of the human organism (Bence Jones, P M [4] 29, 394), and in normal urine (Schiaparelli a Peroni, G 10, 390)

While investigating various silicates in 1817, Arfvedson (S 22, 93, 34, 214) found a new alka line base with a molecular weight smaller than that of soda or potash. Berzelius gave the name lithia to the new base ($\lambda i \theta \epsilon i \sigma s$) supposing that, unlike soda and potash, it was to be found only in minerals. The new alkali was decomposed by electrolysis in 1818 by Davy, also in 1820 by Brandes (S 8, 120), but the metal was first prepared approximately pure and in considerable quantity by Bunsen and Matthiessen in 1855 by

electrolysing fused LiCl (A 94, 107)

Preparation —The metal is obtained by electrolysing molten LiCl Bunsen a Matthiessen (A 94, 107) passed the current from 4-6 Bunsen cells through LiCl kept molten in a thick walled porcelain crucible, using a cylindrical rod of retort graphite as positive electrode, and an iron wire the thickness of an ordinary knitting needle as negative electrode The metal separated on the iron wire in small pellets, which were quickly removed by an iron spoon and placed under petroleum. Some of the metal was always oxi-dised, occasionally with ignition. To obviate this, Hiller (Neues Handwörterbuch der Chemie, 8, 534) passed the negative electrode (iron wire) through the stem of a tobacco pipe, which he connected with an apparatus supplying pure dry H, he allowed H to pass through the pipe until air was completely expelled, then plunged the bowl open end downwards, with the end of the wire inside, into the molten LiCl, stopped the H, and sent the current through the LiCl, when sufficient Li had collected inside the bowl, the pipe was broken and the metal collected under petroleum To prevent any action between the Li and the silica in the pipe, the inside of the bowl is covered with a thin layer of graphite, this is done by mixing powdered graphite with

dilute LiClAq so as to form a thick paste, spreading this inside the bowl, and drying first in air and then at a moderate red heat. It is advantageous to mix the LiCl before fusion with some NH,Cl

There are many methods for preparing LiCl from Li containing minerals, the methods vary according to the composition of the mineral dealt with, all seek to prepare a solution containing only the alkalis, from which Li may be separated by taking advantage of the comparatively small solubility in water of Li CO, LiCl is obtained by dissolving Li,CO, in HClAq, evaporating, and drying the crystals which separate Lepidolite is the usual starting point, different specimens contain from less than 1 to c 5 p c Li₂O The mineral is very anely powdered and triturated with water, the finest powder is dried and heated to redness with twice its weight of 'me, the cold mass, in which the SiO2 is combined with lime, is treated with HClAq, CaO is ppd from the solution by H2SO, Aq and evaporation, the filtrate is evaporated to dryness, and the solid is heated until H2SO, is all removed, the residue is dissolved in water, the solution is digested with CaCO₃, to remove Al₂O₃, and Ca is removed by ppn with (NH₄)₂CO₄, the filtrate is evaporated to dryness, and the residue is strongly heated, the Li-SO, thus obtained is dissolved in water, and the liquid is ppd by Ba acetate after filtration the Li acetate is strongly heated and so transformed into Li CO, (Arfvedson, S 22, 93, 34, 214)

The method recommended by v Hauer (J pr 68, 310) consists in strongly heating for 2 hours a mixture of equal parts of very finely powdered lepidolite and gypsum, lixiviating the mass with water, filtering, evaporating until CaSO, and K2SO, crystallise out, adding to the mother-liquor a mixture of NH₂Aq, NH₂HSAq, and (NH₂)₂C₂O₃Aq, whereby all bases are ppd except the alkalis, after filtering, Li₂CO₃ is ppd from

the warm solution by (NH₄) CO₁

The process adopted in Schering's manufactory at Berlin is described by Filsinger (D P J219, 183, 222, 321, 385) Finely ground and sifted lepidolite is mixed with conc H.SO, in a warm brick trough to the consistence of a thin paste, which is heated with slight stirring till it forms into lumps, the lumps are calcined in a reverberatory furnace, and, while warm, are lixi viated with water, the liquid is mixed with enough K2SO4 to convert all Al2O3 into alum, which separates on boiling, the esidual Al,O, being removed by milk of lime, the salts in the filtrate are converted into chlorides by ppn with BaCl2Aq, and the liquid is evaporated to dryness, digestion with absolute alcohol dissolves the chlorides of Li and Ca, after distilling off al cohol, Ca is ppd by (NH₄),C₂O₄Aq, the liquid is filtered, and a little NH₄HSAq is added to ppt any Fe, &c, still present, the filtrate is boiled to remove NH, HS and evaporated to dryness in a silver dish, pure LiCl is thus obtained LiCl may be conver ed into Li₂CO₃ by dissolving in water, adding NH₂Aq and (NH₄)₂CO₂, and washing the pp with alcohol of 60 p c

Schrötter's method is said to be one of the best (J pr 93, 275) Lepidolite is melted, at full red heat, with frequent stirring, the molten mass is ladled out by an iron spoon into water,

LITHIUM 149

when cold the solid is powdered and triturated with water, HClAq S G 12 is added little by little to the pasty mass, care must be taken that sufficient water is present to prevent the whole mass from solidifying, after standing for 24 hours, with frequent stirring, the semi liquid substance is heated nearly to boiling, and a little more HClAq S G 1 2 is added, the total quantity of HCl used should be c 2 parts to 1 part lepidolite, after a few hours most of the SiO. has separated, a little of the filtered liquid should be so acid that no permanent pp is formed on addition o a few drops of Na₂CO₃Aq, a little HNO, Aq is now added to completely oxi dise FeCl, to FeCl, the liquid is filtered from ppd SiO₂ (which separates as a powder), and Fe₂O₃, Al₂O₃, CaO, MgO, &c, are ppd by careful addition of Na CO, Aq to the boiling liquid The alkaline filtrate is nearly free from all salts ex cept chlorides of the alkalis, it is evaporated until the small quantities of MgCO₂, MnCO₃, &c, still present separate out, and Li,CO, 18 ppd from the filtrate by addition of Na₂CO, and

Commercial Li2CO, generally contains small quantities of salts of Mg, Ca, K, Na, &c, it may be purified by one of the foregoing methods For the other methods of preparing Li₂CO, from lepidolite, &c v Hugo Muller, J r 58, 148, Fuchs, J pr 5, 319, Troost, A Ch [3] 51, 103, Mallet, A 101, 389, Lunglmayr, D P J 171, 293, Allen, J pr 87, 480, Reichardt, D P J 172, 447, L Smith, A 159, 82, Stolba, D P J 198, 225, L de Boisbaudran, Bl [2] 17, 551 detailed criticism of various methods will be found in D P J 219, 183, 222, 271 385

Properties -A silver white metal, very soft, but harder than k or Na, when freshly cut, the surface appears vellowish, when melted and at once pressed between gla-s plates it forms a silver like mirror Li makes a grey streak on paper It may be drawn into wire, but shows very little tenacity Li is the lightest known solid, SG c 59, it swims on rock oil at 186° Is not acted on by dry O at its MP, heated in air to c 200° it burns with a very brilliant white flame May be vapourised in Hat full red heat Li decomposes cold water without itself melting, it combines rapidly with Cl. Br, I, S, O, it burns when heated in dry CO. Li reacts with most acids to form salts, conc HNO, Aq oxidises it with great rapidity, the metal usually melts, and is sometimes ignited In dissolves in liquid NH,, and on evaporation of the NH, it is left unchanged (Seeley, C N 23,

The atomic weight of Li has been deter mined (1) By converting LiCl into AgCl (Arfved son, S 22, 93, Mallet, Am S [2] 22, 349, Troost, A Ch [3] 51, 108, Stas, Nouv R 268), (2) by determining O in Li₂O (Berzelius, P 17, 379), (3) by ppg Li₂SO, by BaCl, (Berzelius, P 17, 379, Heimann, P 15, 482, Hagen, P 48, 361, Diehl, A 121, 97), (4) by determining CO, in Li₂CO₃ (Hermann, P 15, 480, Troost, A Ch [3] 51 108, Diehl, A 121, 93), (5) by converting Li₂CO₂ into Li₂SO₄ (Troost, A Ch [3] 51, 108), (6) by converting LiCl into LiNO₄ (Stas, Nouv R 274); (7) by determining SH of Li (Regnault, A Oh [3] 63, 11)

Ramsay (C J 55, 521) has endeavoured to

determine the mol w of Li by measuring the lowering of vapour pressure of Hg produced by dissolving Li in Hg the results make it pro-bable that the mol w of Li is the same as the This result is based on the assumption that Van't Hoff's law holds good, viz, that equal volumes of dilute solutions contain equal num bers of molecules of the dissolved substances, it also presupposes that the molecular weight of liquid Hg is the same as the atomic weight

As the VD of no L1 compound has yet been determined, the valency of the atom Li in gaseous molecules is not certainly known, but from the close analogy between Li and the other alkali metals there can be little doubt that the atom of

Li is monovalent in gaseous molecules

In is a strongly positive metal, it belongs to the group of alkalı metals, none of which shows any tendency to enter into the negative radicle of salts Li shows closer resemblances to the alkaline earths than are exhibited by any other metal of the alkalis, LiOH, Li₂CO₂, and Li₂PO₄ are much less soluble in water than the corre sponding compounds of Na, K, Rb, and Cs, Li does not form an alum The position and analogies of Li are discussed in the article ALKALIS,

METALS OF THE, vol 1 p 114

Reactions and Combinations -1 Li decomposes cold water rapidly without itself melting Thomsen (Th 3, 227) gives the thermal data [Li, H O,Aq] = 48,970 (to form LiOHAq+H) — Very rapidly oxidised by conc nitric acid-3 Slowly acted on by conc sulphuric acid, rapidly dissolved by dilute H2SO,Aq, also by dilute hydrochloric acid (Matthiessen, A 94, 10) Burns when heated in dry carbon dioxide or sulphuretted hydrogen -5 At temperatures lower than its melting point Li acts on silica, alkaline silicates, iron, gold, silier, and platinum - 6 Combines readily with sulphur, phosphorus, and the halogens

Detection - La compounds give a red colour to a non luminous flame Examination by the spectroscope will detect 000009 mgrms Li present as LiCl (Bunsen) To detect Li in silicates, the powdered mineral is treated with HFAq, the liquid is poured off, and the residue is evaporated with addition of a little H2SO4, the residue is extracted with absolute alcohol, and the liquid is evaporated to dryness, the residue is again treated with absolute alcohol, and this solution is again evaporated, and the residue $(\frac{1}{30} \text{ mgm} \text{ is sufficient})$ is examined in the spectroscope, if the mineral is non-siliceous, the treatment with HFAq may be omitted Li is estimated in the form of Li.SO.

Lithium, antimonate of LiSbO, By adding LiCl to KSbO, Aq (cf Antimonates, vol p 285)

Lithium, borate of LigB4O,, and hydrates with 5H2O, 6H2O, and 10H2O, by adding Li2CO2 to boric soid solution (Arfvedson, A Ch [2] 10, 82, Filsinger, Ar Pn [3] 8, 198, cf Borates, vol 1 p 529)

Lithium, borofluoride of By double decomposition between Ba(BF,),Aq and Tu,SO,Aq and evaporation at 40°, large deliquescent prisms are outsined, al sol water, these crystals are probably LiBF, but they have not been accurately examined (Berzelius)

150 LITHIUM

Lithium, bromide of LiBr H F [Li,Br,Aq] = 91,810 (Th 3, 227), [LiBr,Aq] = 11,850 (Bodisko, J R 1889 [1] 7) S G 3 102 at 17° (Clarke, Am S [3] 13, 293) A white crystalline, very deliquescent, mass tolving Li₂CO₂ in HBrAq and evaporating (Troost, A Ch [3] 51, 103), or by ppg excess of CaBr,Aq by K₂CO₃, after 24 hours adding enough Li₂CO₃ to ppt all the Ca, filtering, and evaporating (Klein, A 128, 239) S 143 at 0°, 196 at 34°, 222 at 59°, 244 at 82°, 270 at 103° (Kremers, P 103, 65)

Lithium, chloride of LiCl S G 2 074 at 3 9° (Schroder, P 106, 226), 1 998 at 0°, 1 515 at M P (Quincke, A 138, 141), S G fused 1 575 (Wernicke, P 138, 141) H F [Li,Cl] = 93,810, [Li,Cl,Aq] = 102,250 (Th 3, 227) S H 282

(Regnault)

Preparation—1 By dissolving Li₂CO₃ in HClAq and evaporating—2 By decomposing Li₂SO₄Aq by BaCl₂Aq, filtering from BaSO₄, and

evaporating

Properties — Crystallises from aqueous solution in regular octahedra, very deliquescent, more so than CaCl₂, tastes like NaCl, melts at dark red heat to a clear liquid, which gives off some Cl and becomes alkaline when heated for a long time in the air, the same change occurs to a slight extent when LiClAq is evaporated E sol alcohol, also in a mixture of ether and alcohol in which KCl and NaCl are nearly insoluble Volatilised at white heat S 63 7 at 0°, 80 7 at 20°, 104 2 at 65°, 115 at 80°, 129 at 96°, 139 at 140°, 145 at 160° Gerlach (Fr 8, 279) gives the following —

SG LiClAq	Pc LiCl		Pc LiCl
1 006	1	1 148	25
1 030	5	1 182	30
1 058	10	1 219	35
1 086	15	1 256	40
1 117	20		

BP of saturated L₁ClAq = 171° (Kremers, **P** 103, 65)

Reactions—1 Heated in air for some time is partially decomposed with evolution of Cl, residue is alkaline (Schulze, J pr [2] 21, 407) Evaporation of LiClAq is accompanied by slight decomposition—2 Completely decomposed by heating in steam, with evolution of HCl, decomposition is rapid in presence of silica, but is prevented by admixture of NH₄Cl (Kunheim, J 1861–140)

Combinations -1 With water to form two hydrates (1) LiCl 2H₂O, obtained as quadratic crystals by evaporating LiClAq under 10° Dried between paper, the crystals become opaque and powdery, when warmed, melts in water of crystallisation, then solidifies, and then the dry LiCl melts again at red heat, (2) by evaporating a solution of LiCl in aqueous alcohol, Rammelsberg obtained the monohydrate LiCl H₂O (P 66, 79) -2 With alcohol to form LiCl 2C2H6O, and with methylic alcohol to form 2LaCl 3CH,O, obtained by evaporating solut on of LaCl in the respective alcohols (Simon, J pr [2] 20, 371) - 3 With platinic chloride, to form Li_PtCl_s 6H₂O, orange-red salt, sol in water, alcohol, and ether-alcohol

Lithium, chromate and dichromate of, v. vol n pp 155, 157

Lithium, fluoride of LiF Small crystalline tablets, by dissolving excess of Li₂O₃ in HFAq, filtering, and evaporating Slightly sol in water, melts at red heat (Berzelius, A 1, 17) SG 2295 at 215° (Clarke, Am S [3] 13, 292) By solution of LiF in HFAq and evaporation, crystals of LiF HF are obtained, when heated LiF and HF are formed Fluckinger (A 87, 261) describes the louble salt 2LiF,SbF, LiF combines with SiF₄ to form the silvcofluoride Li₂SiF₈ (v Lithium, silicopluoride of, p 151)

ov, p 151)
Lithium, haloid compounds of Lithium combines directly with the halogens, the haloid compounds, LiX, are generally prepared by dis solving Li,CO, in 'he respective acids and eva porating As the V D of none of the compounds has been determined, their molecular weights are not known with certainty, but from the close similarities between compounds of Li, K Na, and Cs there can be little doubt that the formula LiX (X=F, Cl, Br, I) expresses the composition of the molecules of the haloid compounds of Li

Lithium, hydrosulphide of ?LiSH Obtained by reducing Li SO, by C, and passing H₂S into a solution of the product Only known in solution (Berzelius, P 6, 439) Thomsen gives HF [Lil, S, H, Aq] = 66,120 (Th 3, 227) Lithium, hydroxide of LiOH Obtained by

Lithium, hydroxide of LiOH Obtained by boiling Li₂CO₃ with CaOAq in a silver dish (Pt cannot be used as it is acted on by LiOH), hil tering, evaporating, and heating to 100° , better by ppg Li₂SO₄Aq by an equivalent quantity of BaOAq, filtering, evaporating, and heating to 100° Also obtained by dissolving Li₂O $(q \ v)$ in H₂O and evaporating Thomsen $(Th \ 3, 227)$ gives H F [Li₁, O, H, Aq] = 117,440, and heats of neutralisation [2LiOHAq, H²SO⁴Aq] = 31,290, [2LiOHAq, H²Cl²Aq] = 27,700 Beke toff $(Bl \ 41,\ 312)$ gives [Li²O, Aq] = 13,000 (to form LiOHAq)

A white crystalline mass which melts when heated, without decomposition, sol in water, but less so than KOH or NaOH, insol in ether alcohol Gmelin obtained small crystals of LiOH by evaporating a solution iniacuo, ac cording to Muretow (B 5, 331) the crystals are a hydrate of lithium hydroxide, LiOH HO (cf Dittmar, S C I 7, 730)

Lithium, iodide of LiI Obtained by saturations.

rating HIAq, containing a little H,PO, with Li2CO2, warming the ppd Li2PO4 with BaI2 and a trace of H2SO4, filtering, adding enough L12CO3 to decompose excess of BaI2 present, filtering again, evaporating, crystallising, and drying by pressure between filter paper (Liebig, A 121, 222) Luebig (lc) also recommends to neutralise half of an HI solution containing a little H,PO, by BaO or CaO, to add the other half of the acid, neutralise by Li₂CO₃, filter from Ba or Ca phos phate and evaporate The crystals are gene rally yellowish from a little separated I, this is removed by quickly pressing between filter paper Lil forms small, colourless, deliquescent crystals SG 3 485 at 23° (Clarke, Am S [3] 18, 293) HF [L1, I, Aq] - 76,100 (Th 8, 227) S 151 at 0°, 164 at 19°, 179 at 40°, 200 at 59°, 263 at 75°, 435 at 80°, 476 at 99°, 588 at 120° (Kremers, P 103, 65) By evaporating a solu tion of Li₂CO₂ in HIAq over H₂SO₄, Ram

melsberg obtained the hydrate Lil 3H,O

Lithium, oxide of Li,O Obtained by burn ing small quantities of Li, in a small iron vessel, in dry O at 200°, cooling in O, and heating in the air to decompose Li peroxide (Troost, A Ch [3] 51, 103) Also prepared by heating Li₂CO₃ with C in a Pt crucible, and by heating Lino, to redness in a Ag dish, best mixed with Cu turnings (H Muller, J pre 58, 148)

A white crystalline solid, S G 2 102 at 15° (Brauner a Watts, P M [5] 11, 60) Not de composed by heating with C or Fe Does not act on Pt at high temperatures, corrosion of the Pt vessel in the preparation of Li₂O indicates the presence of Rb,O or Cs O Reacts with Cl, S, and P Heated in O, Li, 9 is superficially changed to peroxide Thomsen gives [Li2,O,Aq] =166,50 (Th 3, 227), and Beketoff (Bl 41, 312) gives $[L_{1,0},Aq] = 13,000$, hence $[L_{1,0}]$ - 153,520

Lithium peroxide is said to be formed by heating Li₂O, or Li₂CO₂, for some time in air or O, but to be decomposed at a little above the temperature of formation

Lithium, phosphide of According to Troost (A Ch [3] 51, 103) L1 and P combine, when heated together, to form a brown substance which is decomposed by water with evolution

of inflammable P hydride

Lithium, silicofluoride of Li,SiF,2H,O Transparent monoclinic crystals, obtained by adding H,SiF,Aq to Li acetate or carbonate evaporating, treating the residue with water, filtering, and crystallising (Stolba, J pr 91, 456) S 526 at ordinary temperature, sol alcohol, insol ether S G 2 33 Dehydrated at 100°, melts at a higher temperature with evolution of

Lithium, salts of Compounds produced by replacing H of acids by Li The Li salts belong to one series Li,\text{\text{ where } X = 2Cl, 2NO, SO, CO,} ²₃PO₄, &c , they are generally obtained by dis solving Li, CO, in the different acids, some are prepared by double decomposition from LiCl or Li₂SO₄ Most of the salts of Li are sol in or Li,SO, Most of the salts of Li are sol in water, but Li,PO, and Li,CO, are considerably less sol than the corresponding salts of the other alkalı metals, LiOH is also less soluble than the other alkalis (cf Alkalis, METALS OF THE, vol 1 p 114) Few, if any, basic salts of Li are known The chief Lisalts are the following (v CAR BONATES, NITRATES, SULPHATES, &c) Antimonate, arsenati, borates, bromate, carbonate, chlorate, chromates, dithionate, hypochlorite, hypophos pnite, iodate, nitrate and ite, perchlorate, perio date, phosphates, selenate and ites, silicates, ulphates and ite, tellurate and ite, thio-arsenate Lithium, sulphide of Li₂S Li and S

Li and S combine when heated together, the solution in water is yellow from presence of polysulphides Li₂S is obtained by reducing Li₂SO₄ by an equivalent quantity of C at full red heat, excess of C makes the product pyrophoric (Berzelius, P 6, 439) Naudin a Montholon (C R 83, 58) say that Li₂S may be prepared by the long-continued passage of H₂S through Li₂CO, sus pended in water Li₂S is easily sol water and alcohol [Li₂, S, Aq] = 115,260 (Th. 3, 227)

Lithium polysulphides are said to be obtained by melting LiOH with S (Vauquelin,

A Ch 7, 284), they closely resemble the poly sulphides of the other alkali metals

Lithium, sulphydrate of, v Lithium, HY DROSULPHIDE OF, p 150
LITHO-BILIC ACID C_{so}H_{so}O_s MMPM

LITHO-BILIC ACID C_{so}H_{so}O₆ [199°] Occurs, together with lithofelic soid, in Oriental bezoar, and is prepared by decomposing the barium salt with hydrochloric acid and recrystallisation from alcohol Long pale-yellow needles, insol water, v sol alcohol, m sol ether Its alcoholic solution is dextrorotatory It resembles lithofellic and the biliary acids in its behaviour with Pettenkofer's reaction and its distillation products (Roster, G 9, 462, Grattarola, J 1880, 831)—BaA'₂6aq Ppd by adding BaCl₂ to a warm aqueous solution of crude sodium lithofellate, usually a yellowish semi transparent resin, was obtained on one occasion in minute monoclinic crystals

LITHOFELLIC ACID C₂₆H₃₆O₄ [205°] S (alcohol) 3 4 at 20°, 15 at 78° S (ether) 225 at 20° (Göbel) [a]_D = 13 8 at 9 5° (independent of concentration) Forms the chief constituent of some kinds of Oriental bezoars (Gobel, A 39, 237, Ettling, A 39, 242, Wöhler, A 41, 150, Heumann, A 41, 303, Malaguti a Sarzeau, C R 15, 518) The finely powdered bezoars are extracted with boiling alcohol, and the solution evaporated The crude acid then deposited is converted into sodium salt, and then into the Ba salt On recrystallising, barium lithobilate remains undissolved, and the solution of barium lithofellate is then decomposed by HCl (Roster, G 9, 364) Minute hexagonal crystals (con taining aq) (Hoppe Seyler, Vinchow's Arch. 25, 528, Grattarola, J 1880, 831) Insol water Dextrorotatory Its salts are also dextro rotatory, somewhat bitter in taste On distillation it gives off aromatic fumes

Reactions -1 When heated with sugar and H,SO, it gives a crimson colour (Pettenkofer's reaction) (Strecker, A 67,53) -2 Boiling HClAq resimifies it -3 Hot nitric acul gives a yellow acid, C20H2(NO2),O3, which may be crystallised from HOAc

Salts -The sodium salt forms a paleyellow gummy mass, exceedingly sol water and alcohol $[a]_D = +1816$ at 145° —BaA', 10aq large prisms, sol boiling water and alcohol [a]_D = +197 at 15°—AgA' flocculent pp

LITHOSPERMUM ERYTHRORHIZON (M. hara, C. J. 35, 22) The Japanese Kuhara, C J 35, 22) The Japanese prepare a dye called Shikon or Tokio purple from the root of this plant The colouring matter may be ex tracted by exhausting successively with water and alcohol Lead subacetate is added to the latter extract, and the purple pp washed and decomposed by aqueous H₂S. The dye is ex tracted from the dried pp by means of alcohol It is resinous with green lustre. Its composition may be represented by $C_{20}H_{30}O_{10}$ Its alcoholic solution is purple, and shows an absorption spectrum similar to that of alkanet Alkalis turn the solution blue, acids turn it red Baryta gives a purple pp C 0H25BaO10 The dye is readily oxidised to a brown scaly substance, C2H30O15 Bromme forms a product of substitution, C₂₀H₂₁Br₂O₁, With PCl₂ it forms black resincus body, C₂₀H₂₂Cl₂O₁, LITHURIC ACID C₁₅H₁₅NO₂ (?) [205°].

Occurs as magnesium salt in some urinary

calcult of oxen (Roster, A 165, 104) Slender, silky needles M sol boiling water and alcohol -MgA'₂ minute monoclinic prisms, m sol boiling water, v sl sol cold water, insoluble in

LITMUS Obtained chiefly from various species of Roccella, Variolaria, and Lecanora, the same lichens that yield archil The blue colouring matter appears to be developed by fermentation after the mass has been treated with alkaline carbonate (Gélis, Rev Scient 6,

50, J Ph 24, 277)
When 2 pts of Roccella tinctoria and 1 pt of K₂CO₂ are repeatedly moistened with a solu tion of ammonium carbonate, the mass acquires a fine blue colour in forty days The mass 18

then mixed with chalk and gypsum
According to Kane (T 1840, 298), litmus contains azolitmin, spaniolitmin, erythrolein, and erythrolitmin Azolitmin is a reddish brown amorphous powder, which dissolves in ammonia with blue colour, and forms blue and violet lakes Spaniolitmin was not isolated by Kane, but appeared to be light red According to Kane, erythrolem is a red viscid mass, form ing a purple solution in ammonia, while ery throlitmin forms deep red crystalline grains, forming a purple solution in ammonia The method employed by Kane to isolate these sub stances is as follows Litmus is exhausted with boiling water, the residue is acidified by HCl, again washed, and then boiled with alcohol The alcoholic solution is evaporated to dryness, and the residue extracted with ether, which leaves erythrolitmin undissolved The ether leaves erythrolein on evaporation The reddish brown powder left after boiling with alcohol is impure azolitmin

De Luynes (C R 59, 49), by heating orcein with aqueous NH, and Na₂CO, at 70°, obtained a blue substance, which he regarded as the blue

colouring matter of litmus

According to Wartha (B 9, 217), cold alcohol extracts from litmus a red substance, which is not affected by acids, and the residue yields to water the blue colouring matter If the aqueous extract be evaporated, and the residue treated with absolute alcohol and some HOAc, a scarlet dye, turned purple by NH3, is extracted, while the residue is the pure litmus blue, left as a brown powder

A blue ethereal extract of litmus shows an absorption-band at D, a red ethereal extract shows an absorption-band extending to E (Vogel)

An aqueous solution of litmus, kept in a closed vessel, gradually becomes decolourised This is due to the action of a micrococcus, which reduces the colouring matter to a leucoderivative, which is readily re-oxidised by air (Dubois, Bl [2] 49, 963, cf Bellamy, J Ph [5] 18, 488)

According to Förster (Fr 28, 428), litmus is best purified by exhausting with alcohol in the cold, digesting with water, filtering, and evaporating The residue is dissolved in water, filtered, and ppd by a mixture of alcohol and HOAc The pp is washed with alcohol, and the solution, ppn , and washing repeated as long as any reddish-violet substance is removed thereby The pp is then dried, dissolved in water, the solution filtered and ppd by feebly ammoniacal

alcohol The pp is finally washed with alcohol and dried

LIVER OF SULPHUR A name formerly applied to a mixture of the polysulphides of potassium, obtained by heating together K, CO3 and S in a closed vessel (v Potassium, sulphides

LIXIVIATION The application of water to solid mixtures, for the purpose of extracting the soluble parts

LOBARIC ACID C17H16O5 A resmond acid obtained by extracting the lichen Lobaria adusta with ether (Knop, C C 1872, 172) Warty masses, made up of thin plates Insol water and baryta water In aqueous or alcoholic NH₃ it forms colourless solutions, which turn rosered on exposure to air KOHAq forms a yellow solution, turning brown on evaporation.

LOBELINE An alkaloid existing in Lobelia inflata (Bastick a Procter, Ph 10, 270, 456) Obtained by extracting the leaves with dilute acetic acid, and ppg with magnesia Thick, oily mass, decomposed by heat V sol water, alcohol, and ether Narcotic Forms crystal line salts with HCl, HNO₃, H₂SO₄, and oxalic acid Its solutions are ppd by tannin

Lobelia nicotianæfolia contains also a second alkaloid, dissolved by CHCl, from solutions made alkaline by NH, It resembles lobeline in physiological action, and, like it, exhibits no characteristic colour reactions (Dragendorff a

von Rosen, C C 1886, 873)

LOGANIN $C_{75}H_{34}O_{14}$ [215°] A glucoside found by Dunstan and Short (Ph [3] 14, 1025) in the pulp in which the seeds of Strychnes nuv vomica are embedded Extracted by alcohol chloroform, and recrystallised from alcohol Prisms V sol water and alcohol, less sol ether, CHCl₃, and benzene The aqueous solu tion is not ppd by reagents for alkaloids, nor by lead acetate or AgNO, Not coloured by FeCl, HNO₃, or H₂SO₄ and K₂Cr₂O₇ Conc H₂SO₄ gives a red colour on warming, changing to purple Loganin does not reduce Fehling's solution Boiling dilute H,SO, splits it up into glucose and loganetin Loganetin is sol water and alcohol, less sol ether and CHCl, It also gives a purple with H,SO,

LORÂOÑIC ACID C₄₂H₄₈O₂₇ (K) or C₅₆H₆₈O₄₄ a G) Lokarn The colouring matter of (C a G) Lokarn Chinese green, obtained from the berries of the buckthorn (Rhamnus utilis), contains lokaonic acid (Kayser, B 18, 3417, of Cloez a Guignet, J 1872, 1068) Lokao, the commercial article, consists of calcium and aluminium lokaonates It is decomposed by boiling with ammonium carbonate, and on adding alcohol to the filtrate ammonium lokaonate is ppd This is deammonium lokaonate is ppd This is de-composed by oxalic acid Lokaonic acid is a deep blue or bluish black mass, which exhibits metallic lustre when rubbed It is insol water, alcohol, ether, and chloroform In aqueous alkalis it forms a blue solution, changed to red by mild reducing agents, such as H.S. Boiling dilute H2SO, splits it up into a sugar, lokaose, and lokanic acid

Salts -NH,HA" (at 100°) deep blue pp with bronze lustre when dry, sol water, insol alcohol—(NH₄)₂A" similar to the preceding. Begins to lose NH₂ at 40°—K₂A" dark blue powder - BaA" (at 100°) deep blue powder,

insol water —PbA" (at 100°) blue black pp

Lokanic acid C₁₆H₁₆O₂₁ (K) or C₁₈H₁₆O₁₆
(C a G) Lokaëtin Obtained by boiling lokaonic acid with dilute H,SO4, dissolving the pp in NH₄Aq, and ppg with oxalic acid Violet black crystalline powder, which exhibits a bronze lustre when rubbed insol water, alcohol, ether, and chloroform Alkalis form a violet solution At 120° it becomes C₃₀H₃₁O₂₀ H₂SO, dissolves it in the cold, and on adding water a reddish brown powder, $C_{36}H_{26}O_{16}$, is ppd This dissolves in NHMq, and the solution gives, with BaCl₂, a reddish brown pp, BaC₃₆H₂₄O₁₆ Lokanic acid is decomposed by boiling conc KOHAq into phloroglucin and delokanic acid Hot dilute nitric acid forms nitro phloroglucin

Salts -NH,HA" (dued at 100°) bluish black powder, sol water insol alcohol Dyes cotton, silk, and wool deep violet without moi dant Mixed with Na₂S₂O₃ it dyes cotton a per manent sky blue (C a G)—BaA" (dried at 100°) blue black powder, insol water and alcohol PbA" deep blue powder, insol water and

alcohol

Delokanic acid C₁₅H₂O₆ Formed as above Brown powder, insol water, sol alcohol solution in alkalis is cherry red. It reduces Fehling's solution with difficulty in the cold

Lokaose C.H.2O. A sugar formed by hydro lysis of lokaonic acid. It reduces chloride of gold and Fehling's solution in the cold It re duces half as much CuO as glucose

LOPHINE v vol 1 p 474

LOTURINE [234°] Occurs to the extent of 24 pc, together with 02 pc of colloturine and 06 pc of loturidine, in lotur bark from Symplocos racemosa, growing in India (Hesse, B 11, 1.42) The alkaloids are extracted from the bark by hot alcohol, and are converted into acetates Loturine and collecturine are ppd from the neutral solution by potassium sulphocyanide, leaving loturidine in solution The crystalline pp is decomposed by Na₂CO₃, and the alkaloids are extracted with ether and recrystallised from The efflore-cent crystals of loturine are separated mechanically from the non efflor escent crystals of collecturine

Properties -Long prisms May be sublimed Insol water, sol alcohol, acetone, ether, and chloroform Its acid solutions exhibit violet chloroform Its acid solutions exhibit violet fluorescence It gives no colour with FeCl₃, conc H SO, HNO, or bleaching powder followed by ammonia Its hydrochloride forms white prisms The hydrochloride, nitrate, and chromate crystallise in needles The platino-

chloride is a yellow pp

Colleturine Long prisms, may be sublimed Its solutions in aqueous HCl and H,SO, fluoresce Its aurochloride is a yellow amor

phous pp

Loturidine Extracted from the filtrate from the ppd sulphocyanides of loturine and col lcturine by adding NH, and shaking with ether Yellowish brown amorphous mass Forms amorphous salts Its solutions in dilute mineral acids fluoresce violet

LOXOPTERYGINE C H34N2O2 [81°] Occurs, together with another alkaloid and tannin, in red Quebracho bark from Loxopterygium Lorentzii (Hesse, A 211, 274) Extracted by alcohol,

the alcoholic solution being evaporated, the residue treated with aqueous NaOH and the alkaloids extracted with ether The acetic acid solution of the alkaloids is mixed with potassium sulphocyanide, which ppts one alkaloid and leaves the loxopterygine in solution, whence it is ppd by ammonia White amorphous mass, sl sol cold water, v sol alcohol, ether, chloroform, and benzene Its solutions exhibit alkaline reaction Tastes intensely bitter Conc H2SO4 and a lattle K2Cr2O, gives a violet colour

LUPANINE C₁₄H₂₁N O Occurs in the seeds of the blue lupine (Lupinus angustifolius), from which it is extracted by alcohol containing HCl (Hagen, A 230, 370) Viscid yellow liquid with green fluorescence, characteristic smell, and very bitter taste Sl sol water, but separates on warming, m sol cold alcohol, v sol ether and chloroform Not volatile with steam Strongly

alkaline, fuming with HCl

Salts —B'HCl 2aq [127°] M sol water and alcohol, insol ether The base is set free from this salt by kOH but not by NH, B'HI 13aq yellow crystals (from hot water), sol. CS, insol alcohol and ether -B'HCyS aq pale yellow crystals, v sol hot alcohol, sl sol water, insol ether —B'H PtCl, 31 aq —B'HAuCl, splen did yellow needles, sl sol ether, insol water and alcohol

Methylo iodide B'MeI [215°] Crystals, sl sol water, insol alcohol and ether methylo hydroxide is formed by treatment with Ag,O but not with KOH

Methylochloride B'MeCl 2aq Extremely deliquescent crystals, insol ether-B'MeHPtCleaq red crystals, insol ether, sl sol alcohol — B MeAuCl, AuCl, lemon vellow needles

LUPETIDINE v DI METHYL PYRIDINE HEXA-HYDRIDE

LUPINIDINE v LUPININE

LUPININ C₂₉H₃₂O₁₆ Lupinin A glucoside in the buds of the yellow lupine (Lupinus luteus) Extracted by 50 p c alcohol (Schulze a Barbieri. B 11, 2200) Slender yellowish white needles (containing 7aq) Sl sol water and alcohol Alkalıs form a deep yellow solution moniacal solution gives a lemon yellow pp with lead acetate Boiling with water or dilute acids splits it up into glucose and lupigenin

Lupigenin $C_1 H_{12}O_6$ Formed as above Minute yellow needles, insol water, sl sol alco Forms a deep yellow solution in aqueous - NH, A'aq len.on yellow powder

LUPININE C₂₁H₄₀N₂O₂ [68°] (256°) An alkaloid in the seeds of the yellow lupine (Lupinus luteus), and extracted by alcohol containing HCl The extract is evaporated to a syrup, treated with KOH, and shaken with light petro-The petroleum is shaken with aqueous HCl, the solution treated with KOH, and the alkaloid extracted by ether, from which it is recrystallised (Baumert, L V 27, 15, cf Beyer, L V 14, 161, v also lupinidine, infra)

Rroperties — Trimetric crystals, may be dis ed in a current of hydrogen Tastes bitter tilled in a current of hydrogen V sol cold water and alcohol, less sol hot water, v sol benzene, chloroform, and CS₂ Strong base, liberating NH₂ from its salts and fuming with HCl In its solutions tannin gives a flocculent pp , phospho-molybdic and phos154 LUPININE

photungstic acids give yellow pps , iodine gives

a dirty brownish red pp Reactions — 1 HI gives C25H50N2O12 2 With fuming HCl at 200° it forms anhydro lupinine C21 H38N2O and finally di-anhydro lupinine $C_{21}H_{36}N_2$ (Baumert, A 214, 366) —3 P_2O_3 heated with the hydrochloride at 180° forms oxylupinine, which with platinic chloride forms C. H., N. 2O. H. 2PtCl., crystallising in yellow plates If the mother liquor be heated with P₂O₅ to a higher temperature anhydro lupinine is formed (Baumert, A 214, 360) -4 Sodium dissolves in fused lupinine, but the product is decomposed by water into NaOH and lupinine (Baumert, B 15, 631)

Salts -B"H2Cl2 large trimetric crystals crystals, v e sol water and alco B'H₂SO. deliquescent prisms -B"(HAuCl₄)₂ needles, v sl sol B"H₂PtCl 6aq crystals, sol water water -

Acetyl derivative C1H38Ac.N2O2 Ob tained by heating lupinine with AcCl or with Ac₂O and NaOAc (Baumert, A 224, 313) Oil — B"H₂PtCl₆ orange trimetric plates

Methylo-rodide B"Me,I2 white hexa gonal plates, sl sol alcohol (Baumert, B 14, 1221)

Methylo-chloride B"Me₂Cl₂ pearly plates —B"Me₂PtCl₆aq orange red needles -

B"Me Au₂Cl₈ yellow pp Ethylo-rodrde B"Et₂I₂ hexagonal plates (Baumert, B 14, 1321) Decomposed by Ag O, but not by KOH From it may be obtained

Bu'Et, PtCl, aq and B''(EtAuCl,), [70°]

Anhydro-lupunne C, H, N, O Formed by heating lupunne with fuming HCl at 150°-200° (Liebscher, B 14, 1880) Liquid which cannot be distilled Oxidised by air Smells like conine Forms crystalline salts -B"H₂PtCl₆ red tables, v sol water

Di-anhydro-lupinine $C_{21}H_{36}N_2$ (220°) From lupinine and cone HClAq at 200° (Liebscher a Baumert, A 214, 371) Oil Readily oxidised by air -B"H,PtCl, dark red crystals, v sol warm water

Lupinidine $C_8H_{15}N$

Preparation - Lupine seeds are extracted with dilute alcohol acidified with H.SO., and, after as much fat as possible has been removed, the sulphate solution is evaporated to a syrup and the residue triturated with absolute alcohol, when it solidifies to a mass of crystalline plates This mass is again triturated with absolute alcohol, when a white crystalline meal of acid lupinidine sulphate separates The mother liquors are treated again in the same manner, until the residue, on trituration with alcohol, either remains liquid or at least redissolves on washing with absolute alcohol, in this case it consists for the most part of lupinine sulphate The mother liquors containing the lupinine sulphate are freed from alcohol, dissolved in water, and ppd by BaCl₂ The filtrate now contains chiefly lupinine chloride, from which any lupinidine salt present can be ppd as platino chloride (G. Baumert, A. 225, 365). Lupinidine is obtained by decomposing the acid sulphate by one of the stronger bases, shaking with ether, and distilling in a current of hydrogen The fact that this alkaloid distils over in a stream of hydrogen, between the wide limits of 250°-820°.

is explicable on the assumption that the lupin-idine golffom the seeds of the yellow lupine is a mixture of crystallisable hydrate (see below) and a liquid anhydride The formula C₈H₁₅N is calculated from analyses of its salts

Properties -Thick yellow oil of intensely bitter taste and disagreeable hemlock like smell, but this smell is probably due to a decomposition product Strong base Very easily oxidisable by the air when in contact with acids or with KOHAq, but not with NH3Aq Gives no acetyl derivative or ethylo iodide (liaumert, A 225, 365) Lupidine is a feeble poison, acting on frogs like curare (Kobert, A 227, 219)

Salts—B'HCl yellow deliquescent crystals
—B'HI laq rather large crystals resembling alum, v sol hot water, m sol alcohol—B'2HI(?) Formed by heating lupinidine with EtI lupinidine resembles berberine in giving a hydro iodide when heated with EtI (Baumert, A 227, 207) —B'H₂SO, minute crystals, v e sol water, v sl sol alcohol —B',H.PtCl, 2aq trimetric crystals, a b c = 885 1 1 171 (Luedecke, Z K 12, 297), sl sol water, m sol HClAq, v sol dilute

alcohol (Baumert, A 225, 365)

Hydrate C₈H₁₈Naq? The liquid and crys
talline portions of the lupine alkaloid are to be considered as modifications of the same base (the hydra e being crystalline), since both yield the same double salt with PtCl. The existence of a hydrate, stable only in the cold, may also explain why cold aqueous solutions of lupinidine, lupinine, and confine become milky on heating A further proof of the correctness of this view is that the yellow oil only (probably the pure anhy dride C.H., N) was got on treating the lupinidine with P2O, (Baumeit)

Lupinine A crystalline alkaloid, called by this name, was obtained by Bettelli (G 11, 240) by extracting white lupine (Lupinus albus) with alcohol It forms white needles, v sol water An alcoholic extract of the plant has been used with some success in cases of intermittent mala rial fever Solutions of the alkaloid give white pps with tannin, HgCl, and AgNO, in the last case reduction soon takes place Platinic and gold chlorides and pieric acid give canary yellow pps HIAq containing iodine gives a red amorphous It does not reduce Fehling's solution Boil ing KOH gives off ammonia

A liquid alkaloid, also called Lupinine lupinine, was obtained by Campani (G 11, 237) from the white lupine It boiled between 210°

and 218° and was poisonous

The young shoots of the yellow lupine contain an alkaloid called Arginine $(q \ v)$ The danger to sheep from eating lupines appears to be due to another substance 'icterogen,' perhaps pro duced by a parasite growing on the lupines (Baumert, Ar Ph [3] 24, 49, Kobert a Lieb scher, J 1886, 1696, Kuhn, ibid)

LUPULIN The yellow granular aromatic powder situate at the base of the cones of the hop and forming from 8 to 18 pc of the cones It contains hop oil, a resin, a nitro genous substance, a gummy substance, and a bitter principle Lermer (D P J 179, 54) extracted the bitter principle by ether, shook the ether with aqueous KOH, ppd by CuSO₄, decomposed the copper compound with H.S. and recrystallised from ether He describes the 'lupulin' so obtained as large with prisms, insol water, v sol alcohol, ether, and chloroinsol water, v sol alcohol, ether, a form The alcoholic solution, diluted with water, had a bitter taste and acid reaction also obtained a compound [110°] which likewise formed a copper salt Lupulic acid, as described by Bungener, appears to be Lermer's lupulm Issleib (Ar Ph [3] 16, 345) found a 'pseudo glucoside' $C_{*0}H_{46}O_{10}$ which he extracted by cold The extract was treated with animal charcoal, the charcoal dried and exhausted with 90 pc alcohol, and the yellow solution partially, evaporated A brown resin C10H24O3 is deposited while a bitter uncrystallisable substance remains in solution From the aqueous solution of this bitter substance ether extracts only the bitter principle (which amounts to 004 of the hops) and leaves in the water $C_{1n}H_{1n}O_s$, a tasteless product of the oxidation of oil of hops C10H18O The bitter principle, according to Issleib, forms a yellow solution in alkalis, and is split up by boiling dilute H2SO, into lupuliretin CH16O, and lupulic acid C₄₀H₈ O₁₉. This lupulic acid forms a crystalline barium salt BaC₄₈H₈₀O₁₉ 5aq According to Bissell (Ph [3] 8, 508) lupulin does not con tain all the active principle of the hop The bitter principle may usually, but not always, be ppd from an infusion of hops by lead acetate (Allen An 13, 43) According to Hayduck (C C 1887, 694), when hops are exhausted with ether, and after evaporating the ether, the residue is treated with alcohol, a white wax is left behind alcoholic solution gives a yellow pp with lead acetate, and the filtrate contains two resins, one soluble, and the other insoluble, in light petro leum

Lupulic acid C H O [93°]

Preparation—By extracting hop flour with light petroleum spirit, distilling off the solvent, cooling, filtering off the black liquid from the crystals formed, and recrystallising the crude acid from alcohol and petroleum spirit

Properties — Colourless prismatic crystals, rapidly altered by exposure to the air V sol alcohol, ether, benzene, CHCl., CS, and the ethereal oil of the hop, sol petroleum spirit, insol water Easily reduces ammoniacal AgNO₂ Exposed to the air is transformed into a yellowish resin This product of oxidation is all sol water, to which it imparts an intense bitter taste, and this resin is the bitter principle of the hop — CuA' A crystalline powder (Bungener, Bi [2] 45, 487)

LUPULINE v HOPFINE

LUTEIC ACID $C_{20}H_{20}O_{12}$ (?) [274°] S 009 in the cold, 03 at 100° S (alcohol) 4 2 in the cold S (ether) 37 A yellow colouring matter prepared from the flowers of Euphorbia Cyparissias (Hohn, Ar Ph [2] 140, 218) fresh flowers are exhausted with alcohol of 60 pc, the greater part of the alcohol distilled off, and the residual liquid filtered and ppd with basic lead acetate The pp is suspended in water, decomposed by H.S., and filtered The filtrate is evaporated over H.SO,, and the yel lowish crusts that separate are recrystallised from ether-alcohol, and then from hot water containing 4 pc of alcohol Slender yellow Has no smell and a bitter taste needles limes at 220° Its solutions exhibit acid reaction Lutein somewhat resembles luteolin and, like the latter, gives protocatechine acid by potash fusion. It dissolves in caustic and carbonated alkalis forming yellow solutions. It reduces AgNO₃ mercurous nitrate, and Fehling's solution on heating FeCl, gives a green colour, changing to reddish brown on further addition of FeCl, Conc H₂SO₄ dissolves luteïc acid, but water reppts it unaltered Boiling dilute H₂SO₄ does not attack it

LUTEIN This name is given by Thudi chum (Pr 17, 253) to the yellow substance ob tained by Piccoli and Lieben (Z 1868, 645) from the ovary of the cow, and called by them 'hæmoluteïn' (cf Holm, Z 1867, 779) It occurs also in the human ovary The same or a similar substance occurs in butter, yolk of egg, serum of blood, in some diseased swellings, in carrots, &c It occurs also in the retina of the eyes of fowls (Capranica, J Th 1877, 317, Kuhne, J Th 1877, 317) According to Maly (C C 1881, 485, M 2, 359), the lutein in yolk of egg of hens and shrimps is a mixture of vitello lutein and vitello rubin If the yolk is extracted with alcohol, and the extract treated with hot baryta water, vitellorubin is ppd while vitellolutein remains in solution Or the yolk extract may be boiled with a little acid, and the ppd albumen treated with petroleum which extracts vitellolutein, while CS2 extracts vitellorubin from the residue Vitellorubin contains no nitrogen It is red, and forms a Mg compound sol ether, chloroform, and CS2 but ppd by alcohol in red flakes An alcoholic solution of vitellorubin shows a broad but weak absorption band including the line F lutein forms a yellow alcoholic solution which exhibits two narrow absorption bands, one including F, the other between F and G It con tains no nitrogen

LUTEOCHROMIUM SALTS, v vol 11 p

LUTEOCOBALTIC SALTS, v vol n p 228 **LUTEOLIN** $C_{20}H_{14}O_8$ (Moldenhauer, A 100, 180) or (C12H3O3)2 daq (Schutzenberger a Paraf, A Suppl 1, 256) [320°] S 007 in the cold, 02 at 100° S (alcohol) 2 7 S (ether) 16 007 in the cold, The vellow colouring matter of weld (Reseda luteola) (Chevreul, J Chim Med 6, 157) tained by boiling weld with water (16 pts) mixed with alcohol (1 pt), filtering, evaporating. dissolving the yellow flakes in alcohol, and pouring into water It is recrystallised from a mixture of water and glycerin (Rochleder, J pr Yellow, four sided needles in radiate 99, 433) May be sublimed Partially decomgroups posed on fusing Has a slightly bitter, astringent taste Reddens litmus slightly solves with deep yellow colour in caustic and carbonated alkalıs Conc H SO, forms a yellow solution, whence water reppts it Potash-fusion CO2, phloroglucin, and protocatechuic Very dilute FeCl, gives a green pp, excess of FeCl, forms a brownish red solution Alcoholic lead acetate gives a pp C₁₂H_oPbO₃aq
(69-LUTIDINE C₂H_oN Ethyl pyridine (?)
Mol w 107 (166°) S G 2 956 (W), 958

(6)-LUTIDINE C.H., N Ethyl pyrdine (?) Mol w 107 (166°) S G 2 956 (W), 959 (C) V D 3 79 (calc 3 70) S (W) Ob tained, together with homologues, by distilling cinchonine with KOH, a mixture of some ten bases is obtained and these are separated by fractional distillation (Greville Williams, J

1855, 549, 1864, 437, Pr 13, 305, Oechsner de Comneke, C R 92, 413, Bl [2] 35, 296, R T C 1, 132, A Ch [5] 27, 462, 488) The same base appears to be formed by distilling with zinc dust the syrupy acid formed by oxidis ing cinchonine with chromic acid mixture (Weidel a Hazura, M 3, 780) This, or an someric ethyl pyridine, is formed by distilling brucine with KOH (O de Coninck, Bl [2] 42, 100) Liquid, sl sol water, sol alcohol and ether The aqueous solution does not become turbid on warming, the base being more soluble in hot than in cold water It appears to form an unstable hydrate C,H,NH₂O Smells some what like nicotine Physiologically it is a vio lent poison and stops tetanus produced by strychnine (Greville Williams a Waters, Pr32, 162) By chromic acid mixture or by KMnO. it is exidised to pyridine carboxylic (nico tinic) acid [231°] When heated with sodium it appears to form di (\$) lutidine C14H18N2 (Gre ville Williams, Pr 33, 159) Chlorine passed into (β) lutidine containing dissolved iodine appears to form tri-chloro (β)-lutidine Chloro acetic acid gives C₇H₆NClCH₂ CO₂H (163°) forming (C₉H₁₂NO₂Cl)₂PtCl₄ 2aq (Pictet, *J* 1882, 1079)

Salts —B'HCl Very deliquescent crystals —B'HBr —B'₂H₂PtCl₆ orange red leaflets Its pp is not retarded by presence of excess of HCl (difference from bone oil lutidine) Hot water decomposes it forming B'2PtCl4 crystallising in pale yellow leaflets —B'2PtCl2 From platinous chloride (1 pt) and lutidine (1 pt) combina tion takes place with rise in temperature (of 70°), the product being a hard brittle mass (Williams)—B'HAuCl. Yellow pp On boiling with water it forms yellow B'2HAu2Cl, and ultimately B'2AuCl3 a red crystalline powder -B'2H2PdCl, garnet red prisms, obtained by mixing solutions of the hydrochloride and of palladium chloride (W) Decomposed at 100°, giving off HCl and leaving B'2PdCl2, sl sol water -B'2H2Cl2Ur2O2Cl2 Formed from uranyl chloride and (β) lutidine hydrochloride Yellow -B'₂H₂SO₄(UrO)₂(SO₄)₃ From uranyl sulphate and (β) lutidine sulphate Small yellow needles -Picrate B'C₆H₂(NO₂)₃OH Yellow needles (Williams, Pr 33, 159)

Combinations — B'₂CuSO₄ 4aq When (\$\beta\$) lutidine is added to a solution of cupric sulphate a copious pale green pp is formed, which desolves in excess, forming a rich blue liquid, which deposits blue prisms of B'₂CuSO₄ 4aq — B'₂AgNO₄ Formed by ppg silver nitrate solution with (\$\beta\$)-lutidine and recrystallising from alcohol

D1 (3) lutidine When sodium is warmed with (3) lutidine dissolved in toluene a product is obtained from which it is possible to get a platinochloride containing a percentage of platinum corresponding to the formula $C_{14}H_{18}N_1HPtCl_3$ (Williams, C N 44, 308) Tetra-(3)-lutidine When sodium is warmed

Tetra-(β)-lutidine When sodium is warmed with (β)-lutidine a violent action takes place, and from the product a platinochloride may be obtained certaining a percentage of platinum corresponding to the formula C₂₈H₃₆N₄HPtCl₃ (Williams)

Hydride of (β)-lutidine C₇H₁₈N Greville Williams found that sodium amalgam had no

action on (8) lutidine According to Oechsner de Coninck (Bl [2] 42, 121), however a hexa hydride (155°-160°) may be formed by the action of sodium on an alcoholic solution of the base (cf Wyschnegradsky, B 13, 2401) It combines with MeI and the product, when distilled with KOH, yields C₈H₁₇N (160°) It also combines with EtI, and the product treated with potash yields a tertiary base boiling at 175°

Lutidine C,H_uN (173°) Obtained by distilling strychnine with zinc dust (Scichloni a Magnanin, G 12, 445) Yellow hiquid, insolwater, sol alcohol and ether Smells like pyridine Gives with sodium phosphomolybdate a dark yellow pp., sol ammonia Potassio mer curic iodide gives a yellow amorphous pp. Mer curic chloride gives a white pp. Iodine in KIAq gives a crimson pp., insol dilute HClAq

Coal tar lutidines v Di methyl peridine
Isomerides v Ethyl peridine and Di
methyl-peridine

LUTIDINE CARBOXYLIC ACIDS & DI METRYL PYRIDINE CARBOXYI IC ACID

LUTIDINIC ACID v Pyridine-di carboxylic

LUTIDONE v OXY DI METHYL PYRIDINE LUTIDO-STYRIL v OXY DI METHYL PYRIDINE LUTID/L-QUINOLINE v DI MI THYL PYRI DYL QUINOLINE

LYCACONITINE v Aconite alkaloids

LYCINE The base from Lycrum barbarum to which this name was applied has been shown to be identical with betaine

LYCOPODINE C₁₂H₃₂N₂O₃ [115°] Occurs in Lycopodium complanatum (club moss), from which it is obtained by extracting the root with alcohol, evaporating the extract, dissolving the residue in water, adding lead subacetate, removing excess of lead by H S, adding NaOH, and shaking with ether. When the ether is evaporated the alkaloid is left, and may be purified by dissolving in HClAq and ppg with conclusion of the conc

LYCOPODIUM BITTER The alcoholic and aqueous extracts of Lycopodium chamacyparissus are evaporated, and the residues mixed and extracted with water The solution is treated with lead acetate and subacetate, filtered, freed from lead by H₂S and evaporated The residue is then washed with alcohol and dissolved in water From this solution lead subacetate ppts the bitter principle, and the pp is then suspended in water and decomposed by H.S. The filtrate is concentrated, freed from sugar by careful fermentation with yeast, dried, and ex tracted with absolute alcohol, which leaves the bitter principle on evaporation (Kamp, A 100, 300) Slender needles (from water) V e sol Slender needles (from water) V e sol , alcohol, and ether Extremely bitter water, alcohol, and ether Contains no nitrogen Neutral to litmus Colours tincture of iodine orange red Does not reduce Fehling's solution, but after boiling with dilute H2SO, it does so

LYCÓPODIUM OIL The oil from the fresh spores of club moss contains phytosterin C₂₁H₄₂O, together with glyceryl ethers of lycopodie

C18H38O4, oleso, arachic, stearic, and palmitic [acids (Bukowski, Chem Zeit 1889, 174, cf

Langer, Ar Ph [8] 27, 625) LYCORESIN C₀H₁₈O [170°] Extracted from Lycopodium chamæcyparissus by alcohol, and remaining in the mother liquor after lyco stearone has separated (Kamp, A 100, 300) Minute crystals, almost insol boiling water, v sol alcohol and ether, v sl sol cold alkalıs

LYCOSTEARONE C₁₅M₃₀O₂ [75°-100°] amorphous tasteless substance, which may be extracted by alcohol from Ly opodium chamacy

parissus (Kamp, A 100, 300) Insol cold water. sol hot water forming a jelly on cooling sol cold alcohol and ether, v sol alkalıs

A violet dye obtained by pouring LYDINE a solution of aniline (100 g) in fuming HClAq (100 g) diluted with water (120 cc) into a solu tion of K₂FeCy₆ (90 g) in water (850 cc), and heating the mixture to boiling. The product is dissolved in dilute oxalic acid and ppd by alkalıs Violet powder, sol alcohol, sl sol ether and benzene, insol water Poisonous (Guyot, C R 69, 829) Possibly identical with mauvine.

\mathbf{M}

C,H19NO, (?) [201°] MACLEYIN (CHCl_s) 7 S (ether) 1 An alkaloid in Macleya cordata the Japanese Tachiobaku (Lijk man, R T C 3, 182, Ph [3] 13,87) Fxtracted from the root by alcohol and dilute H2SO4, and separated from sanguinarin by ether in which it is very slightly soluble Prisms Almost water and alkalis, v sl sol hot alcohol Almost insol salts have a bitter taste Its chemical proper ties resemble those of protopine Conc H2SO4 gives a faint yellow changing through violet to green Fumes of nitric acid give an ultramarine colour H₂SO₄ and a little K₂Cr₂O₂ give a blue colour

Salts — B'HCl Prisms B'.H.PtCl₆2aq yellowish whitepp -B'.H Cr₂O, prisms - Hydrolodide crystalline -Normal sulphate spheres colourless Thiocyanate needles -Acetate needles needles - Acid oxalate crystals -Acid tarneedles -Benzoate [166°] trate needle

MACLURIN $C_{13}H_{10}O_{6}$ (H a P), $C_{15}H_{12}O_{8}$ Morintarnic acid [200°] (Wagner) 52 at 14° Occurs, together with morin $(q \ v)$, in old fustic, the wood of Morus tinctoria, from which it is obtained by extracting with water The evaporated extract deposits morin, and from the filtrate maclurin may be ppd by HCl (Hlasiwetz a Pfaunder, A 127, 352, J pr 94, 55, Löwe, Fr 14, 117, Benedikt, A 185, 114) Almost pure maclurin is also found in patches in the wood (Wagner, J 1850, 529)

Properties - Yellow, crystalline powder (con-

taining aq), v sol alcohol and ether, sl sol water Above 270° it gives CO, and pyrocatechin Its aqueous solution is ppd by alkaloids, gelatin, and albumen FeSO, gives a greenish black pp Its alkaline solution turns brown in air It dyes mordanted cotton pale brownish-yellow Boiling cone KOHAq gives phloroglucin and protocate chuic acid $C_1, H_{10}O_6 + HO = C_6H_6O_3 + C_7H_6O_4$ Dilute H SO, at 120° does the same Bromine gives tri bromo maclurin C₁₂H₁Br₂O₅ aq minute needles Conc H₂SO₄ at 190° gives brown C₂₂H₁₄O₁₅ (Hlasiwetz, A 143, 308) Reduction with zine and H2SO, gives phloroglucin and When its solution is heated with machronin sodium amalgam and the product acidified, ether extracts phloroglucin and amorphous Cit HisOs, which is sol water and alcohol, is ppd by lead acetate, gives a grass green colour with FeCl₂, and reduces AgNO₂ and Fehling's solution.

Salts - PbC, H,O, aq · yellow crystals -C₁₅H₁ O₇3PbO (L)

Acetylderivative C18H2AcO4 11aq viscid

Machronin C14H10O33aq (?) Formed by the action of zinc and dilute H2SO, on maclurin, and separated from phloroglucin by ppn with lead acetate The pp is decomposed by H2S Colourless spangies composed needles (from dilute alcohol) V sl sol water Turns dark blue less spangles composed of tufts of minute when exposed to air or when heated aqueous solution turns violet blue in air, and then yields an indigo blue pp with HCl FeCl, gives, in a very dilute alcoholic solution, a violetred colour, changing to blue Alkaline solutions AgNO, gives also turn blue on exposure to air a violet colour with reduction of silver Reduces hot Fehling's solution Cone H2SO4 gives an orange solution, turning emerald green on warming or diluting

Rufimoric acid C₁₆H₁₄O₂ (?) Obtained by boiling maclurin with dilute HCl (Wagner, J Obtained by 1851, 420) Dark red mass, v sol alcohol, m sol water, v sl sol ether Forms a crimson

solution in alkalis

MACROCARPINE v THALICTRINE MADDER v OXY ANTHRAQUINONES

MAGDALA RED C_{so}H₂₁N₄Cl Formed by heating naphthalene azo (a) naphthylamine with (a) naphthylamine hydrochloride (Hofmann, B 2, 374, 412) Appears to be a compound of amido-

naphthazine $C_{10}H_3(NH)$ C, H, allied to saf-

franine, viz $C_{10}H_3(NH_2)$ C₁₀H_e (Julius, B

MAGNESIA Magnessum oxide MgO (q v) MAGNESIA ALBA A basic carbonate of Mg, varying somewhat in composition, v CAR-

BONATES vol 1 p 699

MAGNESIA USTA. A name given in pharmaceutical nomenclature to MgO prepared by calcining magnesia alba

-MAGNESIUM At w 24 Mol w probably A 101, 359), [c 500°] (Dute, & R 73, 108), [between 700° and 800°] (V Meyer, B 20, 497) Scarcely volatilises in CO at red to white heat (V. M. Lc.). SG. 169 to 171 at 17° (Kopp);

1 77 at 0° (Wurtz, Am Ch 1876 (March)) S H 20° to 51° 245 (Kopp, T 155, [1] 71) C E at 40° 00002694 (Fizeau, C R 68, 1125) T C (Ag = 100) 84 8 (Lorenz, W 18, 422) E C (Hg at 0° = 1) 22 84 at 0°, 16 34 at 100° (Lorenz, W 18, 422, 582) S V S c 14 1 Characteristic lines in emission spectrum 5527 4, 5183, 5172, 5166 7 (Thalén, Upsala, 1868, v also Liveing a. Dewar, Pr 44, 241)

Occurrence — The metal does not occur native, but compounds of Mg are very widely distributed, and are found in some places in large quantities, they usually accompany Ca compounds Magnesite MgCO,, dolomite a mixture of the isomorphous carbonates of Mg and Ca, kieserite MgSO, H2O, carnallite MgCl2 KCl 6H2O, various silicates e g asbestos (MgCa)SiO,, spinelle MgAl2O,, &c, occur as minerals Borate, phosphate, sulphate, chloride, nitrate, and hydroxide, of Mg are found in mineral waters, and some of them in sea water, Mg compounds, chiefly phosphate and carbonate and compounds of organic acids, are found in plants and animals

Magnesia alba (a basic carbonate of Mg) was introduced as a medicine in the beginning of the 18th century, the name is said to have been given merely in contradistinction to magnesia nigra, a term applied to the mineral pyrolusite because of its colour and supposed magnetic Magnesia was long supposed to be properties the same, or nearly the same, as lime Hoff-mann, Bergmann, Marggraff, and especially Black (1755) established the characteristic properties of magnesia Black showed magnesia alba to be a compound of fixed air (CO2) with an earthy base, to this base he gave the name magnesia In 1800 Davy obtained a small quantity of a metal by reducing magnesia at white heat by vapour of K, in 1830 Bussy ob tained the metal in greater quantity and purity, by heating together MgCl₂ and K

Formation —1 By heating together MgCl₂ and K in a Pt crucible, and washing out KCl by water (Bussy, Buff, P 18, 140, Liebig, P 19, 137) —2 By electrolysing fused MgCl₂ (Bunsen, A 82, 137), or a mixture of MgCl₂ and KCl with a little NH₄Cl (Metthiessen, C J 8, 107) —3 By reducing a molten mixture of MgCl₂, CaF, KCl, and NaCl, by Na (Deville a Caron, C C 1863 993) —4 By reducing MgF₂ NaF by Na (Thisser, C R 56, 848) —5 By electrolysing a mixture of MgSO₄ and (NH₄)₂SO₄ dissolved in water (Gerhard, English Patents, No 16,691, 1884) —6 Puettiner patented a method for reducing MgCO₃ by heating with Fe₂O₃ and (German Patents, No 31,319) —7 Lauterborn reduces a double Mg Na cyanide by Zn (German Patents, No 39,915)

Preparation —1 The upper part of a porcelam crucible is divided vertically into two halves by a thin porcelain plate, the crucible is closed by a porcelain cover, through which pass the carbon electrodes of a battery of 8-10 Bunsen cells, one electrode on each side of the dividing vertical plate, indentations are cut in the negative electrode, the crucible is heated to redness, then filled with fused MgCl₂, and the current is passed through the molten mass. The Mg lodges in the cavities of the negative electrode, and is thus prevented from floating to the surface, the dividing plate serves to prevent contact be tween the Cl, evolved at the positive electrode. and the Mg (Bunsen, A 82, 187) -2 A mixture of MgCl, and KCl, prepared by evaporating a mixture of the salts, in the ratio 4MgCl, 3KCl, to dryness, is mixed with a little NH₄Cl, and is electrolysed when fused in the apparatus de scribed in 1, as Mg is heavier than the molten mixture of salts it is not necessary to form ser rations in the negative electrode (Matthiessen, C J 8, 107) -3 A mixture of 6 pts dry MgCl, 1 pt of a mixture of 7 pts NaCl and 9 pts KCl, 1 pt powdered CaF₂, and 1 pt Na carefully freed from oil, is heated to bright redness in a covered earthen crucible The Mg, which separates in globules, is heated nearly to whiteness in a boat of compact charcoal, placed in an inclined tube of the same material through which is passed a stream of dry H, the Mg condenses on the upper part of the tube, it is then melted into large globules with a flux of MgCl₂, NaCl, and CaF₂ To free the Mg from C, Si, and N, it may be distilled in a current of H at a high temperature (Deville a Caron, A 83, 137, for ar apparatus in which the distillation may be conveniently conducted v Sonstadt, J pr 90, 307) In a later trial D a C ured 7 pts MgCl, 48 pts CaF₂, and 23 pts Na ($C \ \hat{C} \ 1863 \ 993$) -4Wöhler (A 101, 362) reduces a fused mixture of MgCl, NaCl' with excess of NaCl by Na, the mixture is obtained by adding excess of NaCl to MgCl₂Aq and evaporating to dryness The amount of MgCl2 in the mixture must be known in order that the quantity of Na to be used may be calculated, for every 1 pt MgCl, about 1 pt Na should be used

Properties - A silver white, very lustrous, moderately hard, metal, malleable, not very tenacious, may be filed and polished, SG c 175 Mg occludes c 2 its volume of H, by heating in vacuo the H is suddenly evolved Ob tained in lustrous, white, crystals, hexagonal, a c = 11639, isomorphous with Zn (Des Cloi zeaux, C R 90, 1101) Unchanged in dry air, superficially oxidised in ordinary air Heated in air, burns to MgO giving out a brilliant white light, very rich in actinic rays Burns when heated in steam, also in CO2, and in SO. bines directly with the halogens, S, P, As, N Hot water is slowly decomposed by Mg Dissolves readily in dilute acids

Mg is a distinctly metallic element, it forms one series of salts MgX, where X = Cl, NO₃, \(\frac{1}{2} \)SO₄, \(\frac{3}{2} \)PO₄, \(\frac{3}{2} \)Co, \(\frac{1}{2} \) for \(\frac{1}{2} \) each salts, and many double salts, are known. In its chemical relations, Mg is analogous to the alkaline earth metals Ca, Sr, and Ba, and also to the metals Be, Zn, Cd, and Hg MgO and MgO, H₂ are alkaline, MgO H. is formed by the reaction of H₂O and MgO, and is dehydrated to MgO by heat As the V D of no binary compound of Mg with H or one of the halogens has been determined, the valency of the atom of Mg in gaseous molecules is not known with certainty, but from the close similarities between Mg, Zp, and Cd, there is little doubt that the atom of Mg is divalent in gaseous molecules (v Magnesium Group of Elements, pl 163, cf Alkaline earths, metals of the, vol 1 p 112)

The atomic weight of Mg has been determined (1) by determining SO₄ in MgSO₄7H₂O

(Gay Lussac, A Ch [2] 13, 308, Scheerer, P 69, 535), (2) by converting MgO into MgSO, Gerzelius, P 8, 188, Svanberg a Nordenfeldt, J pr 45, 474, Jacquelain, A Ch [3] 32, 202, Marignac, A Ch [6] 1, 289), (3) by converting MgO₂O, 2H₂O into MgO (8 a N lc), (4) by converting MgCO₃ into MgO (Marchand a Scheerer, J pr 50, 385), (5) by determining Cl in MgCl₂ by ppn with Ag (Dumas, A Ch [3] 55, 189), (6) by determining S H of Mg

Molecular weight of magnesium—Ramsay (C J 55, 521) has determined the lowering of vapour pressure of Hg produced by dissolving Mg in Hg, the results make it probable that the molecular weight of Mg is the same as the atomic weight This conclusion assumes the accuracy of Van't Hoff's law, th t equal volumes of dilute solutions contain equal numbers of molecules of the dissolved substances, and it also supposes the molecular weight of liquid Hg to be the same as the atomic weight of Hg

Reactions -1 Slowly oxidised in moist air 2 Decomposes warm water slowly, heated in steam burns to MgO -3 Heated in air or oxygen to above its M P burns to MgO, with bril liant white light, rich in actinic rays -4 Heated in chlorine, bromine, or iodine forms MgCl, MgBr₂, or MgI₂—5 Heated in sulphur forms MgS -6 Heated in nitrogen forms Mg, N, with phosphorus forms Mg,P2, and with arsenic forms Mg, As, -7 Decomposes carbon monoxide and dwxide, also sulphur dwxide, when heated in these gases, forming MgO -8 Reduces ferric chloride and sulphate solutions to 1 eCl, and reso, (Pfeiffer, J pr 61, 441) —9 Reduces nitric acid to HNO₂ (Jenzsch, N T für Mine ralogue 1853 535) -10 Reduces carbonates of the alkali metals except Cs, also oxides of copper, silver, and gold, when heated with them in solid form (Winkler, B 23, 44), also reduces oxides of Ca, Sr, Ba, Zn, Cd, and Hg (W B 23, 120) — 11 Dissolves in delute acids with formation of salts MgX₂, X = Cl \ SO₄, &c, and evolution of H, or N oxides from HNO₅. Cone hot H, SO₄ forms MgSO₄ and SO₂—12. Dissolves in hydroaen peroxide solution with formation of MgO₂H₂. From solutions of salts of copper, iron, man ganese, and cobalt Mg ppts the metals, with evolution of H, from some metallic salts Mg ppts hydrated oxides, eg AlO,H, from solu tions of Al salts, from solutions of salts of arsenic or antimony, Mg evolves AsH, or SbH, -13 Mg forms alloys with most of the metals (v Magnesium, alloys of)

Detection and estimation—Solutions of Mg salts are not ppd by HClAq, H,SO,Aq, H S, or NH,HS Fixed alkalis and their carbonates pt MgO₂H₂ or MgCO₃, insoluble in excess, but soluble in NH, salts, especially in NH,ClAq, hence Mg salts are not ppd by NH,Aq in presence of NH,Cl Na,HPO,Aq, added to Mg salt solutions, in presence of NH,Aq, ppts MgNH,PO₄

Mg is usually estimated by ppn as MgNH, PO, by addition of NH, Aq and Na, HPO, Aq, when strongly heated, the pp is changed to Mg P, O, For details, and methods of separation of Mg from other metals, Manuals of Analysis must be consulted

Magnesium, alloys of Mg forms alloys with most of the metals By reason of the easy

oxidation of Mg, the preparation of alloys of this metal is somewhat difficult. They may be prepared by melting the metals in H, also by melting the other metal and rapidly immersing the Mg in it. According to Parkinson (J. pr. 101, 375), Mg forms alloys with the alkali metals, Al, Sb, Bi, Cd, Cu, Au, Pb, Hg, Pt, Ag, Tl, Sn, Zn, also with Cu and Ni together, but not with Co, Fe, or Ni alone. The alloys of Mg are generally very brittle.

Magnesium, aluminate of, MgAl₂O₄, v Aluminates, vol 1 p 141

Magnesium, antimonate of,

 $Mg(SbO_4)_2$ 12 H_2O , v Antimonates, vol 1 pp 285, 286

Magnesium, arsenates of, v Arsenates, vol 1 p 308

Magnesium, arsenide of Mg,As, Brown mass Formed by heating a mixture of As and Mg turnings in H (Parkinson, J pr 101, 375, cf Arsenic, Combinations No 9, vol 1 p 303)

Magnesium, arsenites of, v Arsenites, vol

1 p 306
Magnesium, borates of, v Borates, vol 1
pp 529,530

Magnesium, boride of According to Phipson (C N 9, 219), a greenish black mass, which is probably a boride of Mg, is produced by heating Mg with boric acid

Magnesium, borofluoride of $Mg(BF_4)_2$ (Ber zelius, P 2,113), v Borofluorides, vol 1 p 526

Magnesium, bromide of MgBr, Mol w unknown, as VD has not been determined Occurs in small quantity in sea water, and in some mineral springs, also in the Stassfurt salt deposits Obtained by passing Br vapour over melted Mg The reaction is very violent (Lerch, J pr [2] 28, 338) A white, very deliquescent, fusible, wax like, crystalline mass By concentrating a solution of MgO in HBrAq, white deliquescent crystals of the hydrated bromide, MgBr 6H,O, are obtained (Rammels berg, P 55, 239), the same hydrate is formed, along with an insoluble oxybromide, by the re action between Mg and Br under water (Lerch, lc) Evaporation of MgBr, Aq to dryness, or heating the crystals of MgBr 6H O, is attended with evolution of HBr and formation of an oxybromide Heated in a stream of O, MgBr₂ 19 entirely decomposed to MgO (Schulze, J pr [2] 21, 407) Kremers (P 108 118) and Gerlach (Fr 8, 285) give the following data for S G, and percentage composition, of MgBr,Aq -

P et MgBr,	SG of solution	Pet. MgBr,	SG of solution
5	1 043	30	1 310
10	1 087	35	1 377
15	1 137	40	1 451
20	1 191	45	1 535
25	1 247	50	1625

The double compounds MgBr KBr 6H₂O and MgBr, NH₄Br 6H₂O are obtained by evaporating mixed solutions of the constituent salts (Lerch, J pr [2] 28, 338)

Magnesium, chloride of MgCl, Mol w unknown, as VD has not been determined

Occurrence —In sea water and in several mineral springs, also in the salt deposits of Stassfurt

Formation -1 The mother liquor, after re-

moving KCl from the Stassfurt salts, is evapoiated to SG 1375 and allowed to orystallise. The crystals of MgCl₂ 6H₂O are heated to melting, whereby they are partially dehydrated, but at the same time some oxychloride is formed. By exposing the crystals to a temperature of c 100° under greatly reduced pressure almost pure MgCl₂ is obtained —2 MgCl₂ is obtained as a by-product in Weldon's process for making Cl, and in Solway's soda ammonia process when MgO is used to decompose NH₄Cl —3 By heat ing MgO with NH₄Cl, adding some NH₄Cl from time to time

Preparation—1 Powdered MgO, or magnesia alba, is dissolved in HClAq, NH₄Cl is added in quantity sufficient to prevent ppn of MgO₂H₂ on addition of NH₈Aq, the solution is made slightly alkaline by NH₄Aq, any silica which separates is filtered off, the liquid is neutralised by HClAq, and evaporated to dryness. The double salt NH₄Cl MgCl₂xH₂O is thus obtained, it is heated to melting (o 460°) in a Hessian crucible, in the bottom of which is placed a smaller Pt dish (Bunsen, A 82, 137), until NH₄Cl is entirely removed, the MgCl₂ collects in the Pt dish at the bottom of the Hessian crucible (cf Dobereiner, S 28, 90)—2 By heating MgCl₂6H₂O in a current of HCl (Hempel, B 21, 897).

The hydrated chloride MgCl₂ 6H₂O is obtained by evaporating the solution of MgO in HClAq to

the crystallising point

Properties — A white, deliquescent, solid, con sisting of a mass of small pearly crystals, SG 2 177 (Playfair a Joule, C S Mem 2, 401) Can be distilled in H at red heat Dissolves readily in water with production of much heat, $[MgCl^2,Aq]=35,920$ (Th 3, 243) Thomsen (lc) gives the thermal data $[Mg,Cl^2]=151,010$, $[Mg,Cl^2,Aq]=186,930$ Sol in alcohol, also in amylic alcohol Gerlach (J 1859 43) gives the following table —

P ct.MgCl_	S G MgCl,Aq	P ct MgClg.	S G MgClaAc
1	1 0084	19	1 1686
2	1 0169	20	1 1780
8	1 0253	21	1 1879
4	1 0338	22	1 1977
5	10422	28	1 2076
6	1 0510	24	1 2175
7	1 0597	25	12274
8	10684	26	1 2378
9	10772	27	12482
10	10859	28	1 2586
11	1 0949	29	1 2690
12	1 1040	30	12794
13	1 1130	31	1 2903
14	1 1220	32	1 3012
15	1 1311	33	1 3121
16	1 1404	34	1 3230
17	1 1498	35	1 8340
18	1 1592		

The hydrate ${\rm MgCl_2~6H_2O}$ crystallises in mono clinic forms, S G 1558 (Filhol, A Ch [3] 21, 415) S 167 cold water, 367 hot water (Casaseas, C R 37, 350) S 20 in alcohol 9 S G, 50 in alcohol 817 S G

Reactions — 1 When the crystals of MgCl₂6H₂O are heated in air, water is given off and at the same time partial decomposition occurs with evolution of HCl and formation of

oxyc_lorides -2 MgCl₂ is partly decomposed by much water to MgO and HCl

Combinations —1 With magnesia to form oxychlorides (v Magnesium, oxychlorides of, p 162)—2 With potassium chloride to form MgCl, KCl 6H,O, occurs native as carnallite, crystallising in rhombic forms according to Marignac (C R 155, 650), in hexagonal forms according to Rammelsberg (Hand der Krystall Chemie, 204) The double salt is prepared by mixing solutions of the constituents in the proper ratio, evaporating, and crystallising -3 With ammonium chloride, and calcium chloride, to form MgCl₂. H₂Cl 6H₂O (v Pfaff a Hantz, A 66, 250), and MgCl₂ CaCl₂12H₂O, respectively — 4 With sodium chloride to form MgCl, NaCl H₂O (Poggiale, C R 20, 1180) — 5 With ferric chloride, and chromio chloride, to form 2MgCl, Fe,Cl, 2H,O, and 2MgCl₂ Cr₂Cl₈ 2H₂O, respectively (Ne₃mann, A 244, 328) —6 With phosphorus oxychloride to form MgCl₂ POCl₃ (9MgCl₂ 10POCl₃ according to Cronander, B 4, 753), a deliquescent solid, decomposed by hot water (Casselmann, A 98, 223) 7 With wodine trichloride to form deliquescent, easily decomposed, crystals of MgCl, 2ICl, 5H2O, obtained by dissolving Mg(IO₃)₂ in conc HClAq, leading HCl into the liquid to saturation, and surrounding by a freezing mixture (Filhol, J Ph 2, 442)—8 With ammonia to form MgCl₂4NH₃, a white sublimate by heating $MgCl_2$ in NH_3 (Clark, A 78, 369)

Magnesium, chromate of, v Chromates,

vol 11 p 155

Magnesium, fluoride of MgF₂ Mol w unknown as VD has not been determined Occurs native as sellatte. Formed by dissolving magnesia alba in Hl Aq, evaporating to dryness, and heating the residue, also by ppg a Mg salt in solution by a soluble fluoride. Obtained in crystals, either by melting the salt, prepared as described, with NaCl or KCl (Cossa, Z K [2] 1, 207), or by melting together 5 parts MgCl₂, 4 parts NaF, and 4 parts NaCl (Roder). Four sided, very hard, white needles. S G 2 856 at 12° (Cossa, B 10, 295). Guntz (A Ch. [6] 3, 5) gives the thermal data [MgO'H', 2HF] = 28,400. Forms a double compound with NaF, vir. MgF₂ NaF. Obtained by adding MgO, H to NaFAq and evaporating, the decomposition according to Tissier (J. pr. 90, 50) is

3NaF + MgO₂H₂ = 2NaOH + MgF, NaF Magnesium, haloid compounds of Mg forms a single compound, MgX₂, with each of the halogens None of these compounds has been gasi fied, hence the molecular weight of none is known with certainty, but the great similarities between Mg, Zn, and Cd, make it extremely probable that the formula MgX₂ expresses the composition of the molecules of the compounds in question MgCl₂, MgBr₂, and MgI₂ crystallise with 6H₂O, when these crystals are heated they are partly decomposed to MgO and HX(X = Cl₂Br, or 1)

Magnesium, hydrosulphide of MgS₂H₂ A solution of this compound is obtained by passing H₂S through MgO suspended in water, the MgO dissolves and leaves a nearly colourless solution, which evolves H₂S when exposed to air or heated The solution thus prepared contains c 16 p c MgS₂H₂, and bas S G 1 118 at 13°

(Divers a Shimidzu, C J 45, 699) MgS₂H₂Aq is also formed by treating MgS with water A solution of MgS₂H₂ is a convenient source of H₂S, a steady stream of the gas is obtained by heating to 60° - 65° (D a S lc) Thomsen gives the thermal data [Mg, S², H², Aq] = 114,880 (Th 3, 243)

Magnesium, hydroxida of $\rm MgO_2H_2$ Occurs native as $\rm brucite$, forming white, pearly, crystaline tablets (hexagonal rhombohedra), S G 2 35 to 2 46 Prepared by ppg a Mg salt by NaOHAq, washing, and drying at 100° , also by direct combination of water with MgO, and drying at 100° , S G 2 36 at 15° (Schulten, C R 101, 72) MgO which has been heated to whiteness does not combine with water (p Deville, C R 61, 975, Knapp, D P J 202, 513, Schwarz, D P J 186, 25, Dittle, C R 73, 111, 191, 270 [Mg,O²,H²] = 217,320, [Mg,O,HO] = 148,960 (Th 3, 243) Soluble c 100,000 parts water, MgO₂H₂Aq is feebly alkaline to litmus, with acids MgO,H₂ reacts as a strong base, forming salts MgV₂, X = Cl, NO₃, $\frac{1}{2}$ SO₄, $\frac{1}{2}$ PO₄, &c, [MgO²H²,H²SO¹Aq] = 31,220, [MgO'H²,2HNO³Aq] = 27,520, [MgO'H²,2HClAq] = 27,520, [MgO'H²,

Magnesium, todide of MgL₂ Mol w unknown as VD has not been determined Obtained by throwing I, in small quantities at a time, on to molten Mg (Lerch, J pr [2] 28, 338), reaction is very violent A white, waxy solid, very de liquescent A hydrate, MgL₂8H₂O according to Lerch (lc), is formed by the reaction between I and Hg under water (L), or by dissolving magnesia alba in HIAq and evaporating over H₂SO₄, very deliquescent MgL₂ is decomposed by heating in air, giving off I, and forming MgO, heated in O it is entirely changed to MgO (Schulze, J pr [2] 21, 407) MgI forms double compounds with KI and NH₂I (Lerch, lc) The following table is given by Kremers (P 108, 118)—

Pc MgIa	SG MgI,Aq	Pc MgI,	SG MgI Aq
5	1 043	35	1 395
10	1 088	40	1 474
15	1 139	45	1 568
20	1 194	50	1 668
25	1 254	55	1 780
30	1.320	60	1 915

Magnesium, nitride of Mg,N2 Mol w un known, as VD has not been determined Ob tained in small transparent crystals by Deville a Caron in making Mg Brieglieb a Geuther (A 123, 236) prepared Mg, N₂ by heating Mg turnings in a stream of dry pure N Mg,N_2 is also formed, according to Mallet (C N 38, 39), when Mg is heated in a small quantity of air Prepared by heating Mg in N, Mg, N, is an amorphous, greenish yellow, powder, becomes brown on heating Heated in air it is slowly oxidised to MgO, the oxidation is rapid when O is sub stituted for air With water, forms MgO and NH, With dilute acids, forms Mg salts and NH, salts Heated in HCl, MgCl, and NH,Cl are formed. Heated in dry H₂S, MgS and (NH₄)₂S are slowly formed Heated to redness in OO or CO₂, MgO, C, and C₂N, are produced PCl₃ vapour reacts to form MgCl₂ and P nitride Vol. III.

Magnessim, oxide of. MgO (Magnessa) Mol w unknown, as compound has not been gasified SG 3 642 at 12° (Cossa, B 10, 1747), SG crystallised 3 636 (Ebelmen, J 4, 15), for SG of MgO heated to temperature from 350° to bright redness v Ditte, C R 73, 111, 191, 270

A new medicine was introduced in Rome in the beginning of the eighteenth century, the name magnesia alba given to it is supposed to have been suggested as a distinction from magnesia nigra, a term then applied to pyrolusite, MnO. The preparation of the new medicine was kept secret. In 1709 Slevogt showed that magnesia alba could be obtained by ppg the mother liquor from the preparation of saltpetre by K.CO. Magnesia alba was supposed to be the same as lime, but Hoffmann found that some of its reactions differed from those of this compound. In 1755 Black demonstrated magnesia alba to be a compound of CO. with a new earthy base, to which he gave the name magnesia

Occurrence —MgO occurs as percelase, crystallised in regular octahedra, SG 3 67, usually coloured green from presence of a little FeO

Formation—1 By adding NaOHAq or KOHAq to solution of a Mg salt, washing, and strongly heating the pp of MgO H₂—2 By cal cining magnesia alba, a basic Mg carbonate ob tained by ppg a Mg salt by an alkaline carbonate (v Carbonates, vol 1 p 699)—3 By burning Mg in O—4 By decomposing MgCl₂Aq by calcined dolomite, MgCl₂Aq + CaO MgO = 2MgO + CaCl₂Aq —5 In crystals same as periclase, by strongly heating powdered MgO in a slow stream of HCl gas (Deville, A 120, 183), also by heating powdered MgO in a porcelain oven (H Rose)

Preparation—1 A boiling solution of pure MgSO, 7H_O, is pad by Na_CO_AAq, after boiling for a little the pp is washed and dried, and the product (4MgCO_3 MgO_H xH_O) is calcined in a Pt vessel until every trace of CO_2 and H_O is removed—2 Magnesia alba is treated with enough dilute HNO_AQ to dissolve nearly but not quite all, after standing for some time in the air with frequent stirring, to ppt Fa_O_xXH_O, the liquid is filtered, the filtrate is mixed with a little pure MgSO_3 alcohol is added, and, after digesting for some time with pure CaSO_3, the liquid is evaporated to crystallisation, and agair filtered, finally the filtrate is evaporated to dry ness, the Mg(NO_3) thus obtained is calcined, the residue is very thoroughly washed, and again calcined (Wurtz) (For preparation of pure MgO from magnesite v Caron, C R 66, 840)

Properties —A white powder, more or less floculent according to the temperature and length of time it has been heated MgO absorbs water and CO₂ from the air, slowly forming MgCO₂ xMgO₂H₂ yH₂O It is slightly soluble in water, 1 part requires 55,368 cold or hot water for solution according to Fresenius, 100,000 to 200,000 according to Bineau. The solution of MgO is feebly alkaline to litmus. When very strongly heated MgO does not melt but gives out a very clear white light. Made into a paste with a little water, MgO sets to a hard, white mass (Deville, C. R. 61, 975), MgO which has been heated to whiteness does not set with water (v. Knapp, D. P. J. 202, 513, Schwarz, D. P. J. 186, 25). MgO reacts with acids as a strong base

forming salts MgX_2 , X = Cl, NO_2 , $\frac{1}{3}SO_4$, $\frac{1}{3}PO_4$,

Reactions -1 With water to form the hydroxide MgO₂H₂.—2 Heated with ammonium chloride NH, is evolved and MgCl₂ formed —8 With acids MgO reacts as a strong base forming salts MgX₂, X = Cl, \(\frac{1}{2}SO_4, &c -4 \) With salts of heavy metals MgO reacts similarly to CaO, BaO, and SrO, ppg hydrated oxides — 5 With and SrO, ppg hydrated oxides — 5 With carbon dioxide and water, basic carbonates MgCO, xMgO H, yH₂O are formed — 6 Sus pended in water through which is passed a current of hydrogen sulphide, a solution of MgS2H2 18 obtained (v Magnesium, hydrosulphide of, p 160) —7 Heated in carbon disulphide vapour, MgO MgS is formed (Reichel, J pr [2] 12, 55)

Magnesium, oxychlorides of When freshly heated MgO is moistened with MgCl2Aq, S G 1 16 to 1 26, the whole sets to a firm, hard mass, which probably consists of a mixture of oxychlorides xMgO yMgCl₂ (v Sorel, C R 65, 102) By warming 30 parts MgO with 1500 parts MgCl, in solution, in an atmosphere free from CO, needle shaped crystals slowly form, when washed free from MgCl₂, pressed, and dried over soda lime, the crystals are 10MgO MgCl₂ $18H_2O$, dried at 110° they lose $4H_2O$ (Krause, A 165,38)

Magnesium, oxysulphide of

 $Mg_2OS(=MgO MgS)$ An amorphous, reddish, solid, obtained, along with COS, by passing CS2 vapour over heated MgO (Reichel, J pr [2] 12,

Magnesium, phosphide of Mg,P, A hard, brittle, steel grey solid, obtained by heating molten P with Mg in H (Parkinson, C J [2] 5, 127, 309), or in a sealed glass tube (Emmerling, B 12, 152) Decomposed by water, evolving PH, and forming MgO, with acids gives Mg salts and PH.

Magnesium, salts of. Compounds obtained by replacing H of acids by Mg The salts of Mg belong to one series, MgX₂, where X = Cl, NO₃, $\frac{1}{3}$ SO₄, $\frac{1}{3}$ CO₂, $\frac{1}{3}$ PO₄, &c A few basic salts, and many double salts, of Mg are known MgCO₃, the basic carbonates and phosphates, and a few other salts are insoluble in water, but most of the Mg salts readily dissolve in water The salts are usually prepared by dissolving MgO, MgO₂H₂, or MgCO₃, in the various acids, and evaporating, some are prepared by double decomposition from the soluble salts, generally from MgSO. As none of the salts of Mg has been gasified the formulæ given are not necessarily molecular, they are based on the results of analysis and considerations of the similarities between the salts of Mg, Zn, and Cd (v MAGNESIUM GROUP OF ELEMENTS) The Mg salts are numerous, and as a class very definite and stable bodies, the fol lowing are the chief salts derived from oxyacids -bromate, carbonates, chlorate, dithionate, hypochlorite, hypophosphite, iodate, nitrate and -te, perchlorate, todates, phosphates and ste, selenate and ste, selecates, sulphate and ste, tellurate and ste, throsulphate (v Carbonates, NITRATES, SULPHATES, &c)

Magnesium, selenide of A flesh coloured pp, probably a selenide of Mg, is obtained by adding K2Se to solution of a Mg salt, the p. 18 decomposed by heat, and by acids, with separa tion of Se (Berzelius)

Magnesium, silicides of A compound of Mg and Si is prepared by placing a layer of fused and powdered NaCl in the bottom of a Hessian crucible, adding one half of a mixture of $2\frac{1}{2}$ parts NaCl and 7 parts Na₂SiF₆, then $2\frac{1}{2}$ parts Mg, and then the other half of the mixture of NaCl and Na, SiF, covering the whole with NaCl, and heating in a wind furnace, when the reaction is completed the contents of the crucible are stirred with a polcelain rod, and allowed to The regulus formed at the bottom of the crucible is a mixture of Mg and Mg silicide, by washing with NH ClAq the Mg is dissolved out (Geuther, J pr 95, 424) As thus prepared the silicide has the composition Mg₈Si₂ It forms metal like, lustrous crystals Reacts with HClAq to form MgCl₂, C1H₄, H₂S1O₃, and H This sub stance may be a compound, or a mixture, of Mg₂S₁ and MgS₁ (Mg₃S₁ = 2Mg₂S₁ + MgS₁) A silicide Mg2Si is obtained by pulverising, in a warm mortar, 40 parts fused MgCl₂, 35 parts Na₂SiF₆, 10 parts NaCl, adding 20 parts Na in small pieces, and projecting the mixture into a hot Hessian crucible After fusion and cooling, the greyish black mass in the crucible is found to contain metal like tablets and globules, these consist of Si and Mg₂Si, by treating with HClAq Si remains and SiH, is evolved (Wohler, A 107, 113, cf Martius, A 107, 112)

Magnesium, silicofluoride of MgSiF, said to be obtained as a gum like, very soluble substance, by dissolving MgO in H,SiF,Aq (Berzelius)

Magnesium, sulphydrate of, v Magnesium,

hydrosulphide of, p 160

Magnesium, sulphides of MgS has been isolated, polysulphides, probably MgS, MgS, and MgS, seem to exist in the solution obtained by warming MgS with S and H2O

MAGNESIUM MONOSULPHIDE, MgS Produced by passing H laden with S vapour over red hot Mg (Reichel, J pr [2] 12, 55, cf Parkinson, C J [2] 5, 125, 309) According to Fremy, MgS is formed, along with CO,, when MgO is strongly heated in dry H_s S, but Reichel (l c) says that the products of this reaction are MgO MgS and COS MgS is also said to be formed, along with $(NH_4)_2S$, by heating Mg_3N_2 in dry H_2S (Briegheb a Geuther, A 123, 236) Fremy (A Ch [5] 38, 324) gives $[Mg_3S] = 39,800$ MgS is formed, but only in very small quantity, by strongly heating MgSO, with C Alkaline sulphides do not ppt MgS, but MgO₂H₂, from solutions of Mg salts

MgS, formed by heating Mg and S, is described as a yellowish grey amorphous, or as a reddish brown crystalline, mass, analysis always gives rather more S than required by MgS water, MgS is decomposed to MgO2H2 and MgS₂H₂Aq, the latter being afterwards converted into MgO₂H₂ and H₂S

By warming, MAGNESIUM POLYSULPHIDES not boiling, MgS and S with water, a dark yellow solution is obtained, containing Mg and S in a ratio varying from Mg 3S to Mg 5S (Reichel, J pr [2] 12, 55) The solution decompos air, giving off H₂S and ppg MgO₂H₂ and S Magnesium, sulphocyanide of, The solution decomposes in

Mg(SCN), 4H₂O, v vol 11 p 350

MMPM MAGNESIUM ETHIDE Mg(C2H3)2 nesium filings act rapidly on ethyl iodide, gas being given off If the product be heated in a sealed tube at 125° the contents solidify to a white mass which on distillation gives off MgEt, and leaves a residue of MgI₂ (Cahours, A 114, 227, 354, Hallwachs a Schafarik, A 109, 215) These statements are contradicted by Löhr (A 161, 48), who finds that EtOAc must be added to the mixture of Mg and EtI, and that the resulting magnesium ethyl is a non volatile solid.

MAGNESIUM GROUP OF ELEMENTS—
Beryllium, Magnessum, Zinc, Cadmium, Mercury Of these five metals, only Zn and Hg
are found native, and these in small quantities
Be occurs chiefly as silicate in combination with
Al silicate, not widely distributed, Mg salts,
especially MgCO, and MgSO, ar found in large
quantities, the chief ores of Zn are ZnCO, and
ZnS, they occur fairly widely distributed and in
considerable quantities, small quantities of
CdS and CdCO, accompany many Zn ores, the
chief ore of Hg is HgS, which is found only in

a few localities Be is classed with the rare elements, approximately pure Be was not prepared until 1885 Mg was obtained by Davy, in small quantity and impure, in 1800, in 1830 Bussy prepared the metal in a state of approximate purity Although brass has been made for very many centuries, yet it was not till the middle of the eighteenth century that the art of preparing metallic Zn was known in Europe. Cd was discovered and prepared in 1817 by Stromeyer Hg has been known certainly from the beginning of the Christian era

Be and Mg are prepared by reducing the chlorides MCl₂ by Na or K, ZnO and CdO are reduced by heating with C, Hg is prepared from HgS by heating with CaO, whereby CaS and CaSO₄ are formed and Hg is vapourised, or by heating with scrap iron, when FeS, SO₂, and Hg

are produced

The following table presents some of the prominent physical and chemical properties of the magnesium metals —

,	BERYLLIUM	Mag~esium	Zinc	CADMIUM	Mercury			
Atomic								
werg hts	9 08	24	64 9	1117	1998			
Melting	heats have be	One or more compounds of each element, except Mg, have been gasified Specific heats have been directly determined Molecular weights of Zn, Cd, and Hg, and probably also of Mg, are the same as the atomic weights						
points	_	700°-800°	4 30°	320°	-39°			
(approx) Sp gr	1 85	17	7 2	87	13 5			
(approx) Sp heats At w	62	245	094	056	033			
Sp gr	4 92	14 1	9	128	14 8			
(approx)	! D	M-00 M-00	7-0 7-93	Commonned &	Tra found notice			
Occurrence and pre paration	Double silicate of Be and Al, and a compound of BeO and Al,O ₃ , oc cur in a few rocks in small quantities Prepared by reduction of mol ten BeCl ₂ by Na, not by electrolysis of BeCl ₂ .	MgCO, MgSO, MgCl, and Mg silicates occur in large quantities and widely distributed Prepared by reducing molten MgCl, by Na, also by electrolysis of MgCl,	ZnCO _s are fairly widely distributed, Zn	quently found accompanying	Hg found native in small quantities Chief ore is HgS, found in a few localities in fair quantity Prepared by heating HgS in air, or with Fe, or CaO, and condensing Hg.			
Physical properties	Steel - coloured, hard, hexa gonal crystals, lustrous	Silver - white, very lustrous, moderately hard, malle-able, not very tenacious Crystallises in hexagonal forms, isomorphous with Zn Melts at temp much higher than MP of Cd or Zn, has not been gasified at white heat	White, with tinge of blue, crystallises in heragonal forms, soft; brittle at ordinary temperatures, malleable at 100°—150°, bittle again at 200° Flexibility varies with temp Melts at c 430°, can readily be distilled.	slight tinge of blue, crystal- lises easily in regular forms, soft, but harder than Zn, very malleable, duc- tile, and flex- ible Vapour is yellow Melts at moderate temperature, c 820°, distils at lower temp	at c 350° Vola- tilises even at			

TABLE-cont

TABLE—CONV								
	BERYLLIUM	Magnesium	Zinc	CADMIUM	MERCURY			
Chemical	Scarcely changed by heating in air or O, burns in O H flame to BeO Scarcely acted on by S at red heat Burns in Cl to BeCl. Dissolves slowly in acids to form salts Only one series of salts known, BeX. where X = Cl, \$804, \$704, &c Dissolves slowly in alkali solutions, evolving H Distinctly positive metal, does not show allo tropy, BeO has no acidic properties Atom of Be is divalent in gaseous molecules.	Unchanged in dry air, heated in air, or O, burns to MgO Decomposes hot water slowly, burns when heated in steam, forming MgO Decom poses CO ₂ at red heat Combines directly with halogens S, P, As, and N Dissolves in acids to form salts Only one series of salts is known, MgX ₂ , &c MgO ₂ H. is a strong base, compounds of Mg do not show any acidic properties Valency of atom of Mg not cer tainly known, as no binary haloid compounds have been gasified Mol w probably same as at w	Unchanged in air, heated strongly in air, or O, burns to ZnO Decomposes steam at red heat Com bines directly with halogens, but not with S Slowly soluble in alkali solution, with evo lution of H Dissolves in acids to form salts One series of salts known, ZnX ₂ , X = Cl, &c ZnO ₂ H ₂ dis solves in alkalis, but is ppd again on eva poration over H,SO ₄ invacuo There are indications of existence of a hydride of Zn Atom of Zn is divalent in gaseous mole cules Mol w same as at w	Slowly oxidised on surface in air, heated in air or 0, burns to CdO Cd vapour and steam heated together form H and OdO Combines directly with halogens, also with S and P Dissolves in acids to form salts Onlyone series of salts known, CdX, X = Cl, &c CdO,H ₂ is not soluble in alka his No compound of Cd shows any acidic proper ties Atom of Cd is divalent in gaseous molecules Mol w same as at w	Unchanged in air, heated nearly to BP is slowly oxidised to HgO Does not de compose water or steam Combines directly with halogens and S Dis solves in acids to form salts Two series of salts are known, HgX and HgX2, X = Cl, &c , salts of both series are numerous and stable HgO dissolves in molten KOH to form K2O 2HgO, HgS dissolves in Na or K sulphide solution to form compounds xNa,SyHgS forms very many ammonio - compounds Atom of Hg is mono and di valent in gascous molecules Mol w same as at w			

General formulæ and character of compounds Oxides -MO, also in case of Hg, Hg₂O Oxides —MO, also in case of rig, rig, of Hydroxides —MO₂H₂ Sulphides —MS, also in case of Hg, Hg₂S Haloid compounds —MX₂, also in case of Hg, HgX Salts —MX₂, also in case of Hg, MX, X = NO₃, ClO₃, ½CO₃, ½CO₄, ½CO₅, ½CO₆, ½CO₇, ½CO₈, ¼CO₈, ¼CO

acids to form salts MX_2 , $X = NO_3$, $\frac{1}{2}SO_4$, &c MgO reacts with water to form MgO₂H₂, the other hydroxides MO H2 are formed by ppg solutions of salts by alkalis HgO shows feebly marked acidic properties, it dissolves in molten KOH, and the compound 2HgO K₂O is obtained on cooling ZnO₂H₂ is sol KOHAq, but is reppd on evaporation in vacuo over H₂SO₄ Mercurous oxide Hg2O is the only representative of the class M2O, it is very easily resolved into Hg and HgO, it reacts with dilute acids, in the cold, as a basic oxide, forming salts HgX Hg2O in some respects resembles Cu₂O and Ag₂O, and exhibits the relations of Hg to the copper group

by heat to MO and H2O, HgO,H2 if it exists is extremely easily separated into its oxide and H2O, the only hydroxide obtained by direct re action between MO and HO is MgO,H, The hydroxides are basic, MgO2H, is slightly

The sulphides MS are basic The existence of BeS is extremely doubtful, MgS is readily decomposed by water, giving MgS,H,Aq, and finally MgO,H₂ and H₂S, ZnS, CdS, and HgS are more stable than MgS, HgS shows slightly acidic properties, it dissolves in K.SAq or Na₂SAq to form compounds xK_2SyHgS Mercurous sulphide Hg2S is very easily decomposed to HgS and Hg

The halord compounds MX2 may be obtained by the direct union of the elements, the mercurous compounds HgX are also obtained in this way MX2 and HgX are also prepared by dissolving the corresponding oxides in HXAq and evaporating, but MgCl, cannot be thus obtained, as evaporation towards dryness of MgCl,Aq re-(v COPPER GROUP OF ELEMENTS, vol 11 p 250). sults in formation of HCl and MgO mixed with The hydroxides MO₂H₂ are all decomposed oxychlorides xMgO yMgCl₂ The compounds BeCl, BeBr, ZnCl, CdBr, HgCl, HgI, and probably HgCl, have been vapourised without de-The haloid compounds form composition many double compounds They all combine with NH₃, various ammonio derivatives of HgX₂ and HgX are known Numerous oxyhaloid com pounds, xMO yMX2, are known

The salts MX2 are numerous and well marked, they are obtained by dissolving the corresponding oxides or carbonates in acids, and evaporating Mercurous salts HgX are prepared by digesting excess of Hg with the various acids Many basic salts of Be, Zn, and in the cold Hg have been prepared, most of the salts of Mg

are normal

The five metals Be, Mg, 7n, Cd and Hg belong to Group II, as the elements are arranged in accordance with the periodic law The following table shows their positions in the Group -

Even Serves

The properties of Be, the first mentoer of the group, suggest those both of the even and odd series members Physically it approaches Mg, Zn, and Cd more than Ca, Sr, and Ba, in the conditions under which it is oxidised, the basic but non alkaline character of its hydroxide, the existence of many basic salts, &c, Be shows closer resemblances to Zn, Cd, and Hg than to Ca, Sr, and Ba The solubility of BeO2H2 in KOHAq also suggests the solubility of ZnO₂H₂ in KOHAq, and of HgO in molten KOH, the hydroxides of Ca, Sr, Ba, and Mg are quite insoluble in alkalis Mg is closely related in many respects to the metals of the alkaline earths, Ca, Sr, and Ba, but its much greater stability in air, its non decomposition of cold water, the easy resolution of its hydroxide into MgO and H O by heat, &c, exhibit the analogies between Mg and Zn, Cd, Hg Sulphides of Ca, Sr, and Ba are readily formed, but MgS is only produced by heating Mg to redness in H laden with S vapour, the difficulty of forming MgS recalls the nonisolation of any compound of Be and S Alkalı carbonate solutions ppt MCO, from solutions of salts of Ca, Sr, and Ba, but the pps obtained from Mg salts are basic carbonates xMgCO, yMgO,H2 The sulphates of Ca. Sr. and Ba are reduced to MS by heating with C, but MgSO, is scarcely, if at all, reduced in this way Hg is distinguished from the other members of the magnesium family by its physical properties, the formation of two series of salts, the formation of a large number of ammonio-derivatives of both series of Hg salts, and in other ways

In the composition of their salts, and sometimes in the isomorphism of salts, the metals of the Mg family resemble those of the Fe family, viz Mn, Fe, N1, Co (v Iron GROUP OF ELEMENTS, For a further treatment of the elements of Group II v CLASSIFICATION, vol 11 pp 204-207, of also Alkaline marths, metals of the, vol i p 112

M M P. M

MAGNETIC ROTATORY POWERS of liquid compounds, v Physical methods, section Optical methods

MAIROGALLOL C₁₈H,Cl₁₁O₁₀(?)[190°] (From μαίρω, I glitter) Obtained, together with leuco gallol, by passing chlorine through pyrogallol (15 g) dissolved in 60 p c acetic acid (45 g) until the liquid is brown, and allowing the liquid to stand (Groves, A 179, 237, Stenhouse a Groves, C J 28, 706, Webster, C J 45, 208) Tri metric prisms, insol water, v sol hot alcohol, extremely sol ether, insol CS, and petroleum ether Decomposed by boiling with water yielding CO, oxalic acid, and tri chloro pyrogallol. Reduced by zinc and H₂SO₄ to tri chloro pyrogallol (Webster, C J Proc 3, 130, Hantzsch a. Schniter, B 20, 2033) Bolling with dilute H₂SO, gives a condensation product, and also a substance that is ppd from aqueous solution by Aqueous NaHSO, and zinc dust reduce it to tri chloro pyrogallol and an amorphous substance which yields furfuraldehyde when distilled with dilute H2SO, Mairogallol gives a crimson colour with solution of sodium sulphite (Cross a Bevan, C J 43, 18) Mairogallol when gradually heated gives a sublimate of tri chloro quinone and tetra chloro quinone These reactions indicate that mairogallol is derived by condensation from CO CCI CCI CCI CCI

(Webster)

MALACHITE GREEN v TETRA METHYL-DI-AMIDO TRI PHENYL-CARBINOL

MALAMIC ACID v MALIC ACID

MALEIC ACID C,H,O, ve CO₂H CH CH CO₂H Mol w 116 (confirmed by Raoult's method, Paterno, B 21, 2158) R_{∞} 386 (in a 69 p c aqueous solution, Kanonnikoff, J pr [2] 31, 347, cf Knop, A 248, 175) H C v 331,702 (Louguinine, C R 106, 1290) H C v 326 900 (Stohmann, Kleber a Langbein, J pr [2] 40, 217) HC p 326,300 (S K a L) HF 187,700 (S K a L) Heat of solution -4,438 (Gal a Werner, Bl [2] 47,158) Heat of neutralisation 26,648 (G a W)

Formation -1 Together with fumaric acid (q v) by the distillation of malic acid (Lassaigne, A Ch. [2] 11, 93, Pelouze, A Ch. [2] 56, 72, Liebig, A 11, 276, Buchner, A 49, 57, Kekulé, A Suppl 1, 129, 2, 85, Von Richter, Z [2] 5, 453) -2 By heating silver succinate at 180° (Bourgoin, C R 72, 52) -3 By saponification of the ether obtained from di chloro acetic ether by heating with reduced silver at 220°, or by the action of sodium upon its ethereal solution in the cold (Tanatar, B 12, 1563) -4 By the action of KCN on a di bromo propionio acid (Tanatar, B 13, 159) —5 From (δ)-bromo pyromucic acid and dilute HNO, (Hill a Sanger, A 232, 55) -6 By the action of baryta on tri-

chloro phenomalic acid CH C(OH) CCl,?

Preparation - Malic acid is rapidly distilled until the residue thickens, the flame being then withdrawn, the distillation then continues by itself until the residue is solid (furgaric acid) The distillate consists of maleic acid and maleic annydride, and may be wholly converted into maleic anhydride by AcCl The maleic anhydride may be purified by crystallisation from HOAc and then converted by hot water into maleic acid (Anschutz, B 12, 2281, cf Perkin,

B 14, 2547)

Properties — Monoclinic prisms V sol water and alcohol, m sol ether Its aqueous solution reddens litmus strongly Begins to boil at 160°, being then restored into maleic anhydride and water, which partially re unite in the receiver An aqueous solution of maleic acid is ppd by baryta (difference from fumaric acid) Unlike fumaric acid, maleic acid is not ppd by adding mineral acids to solutions of its salts

Reactions — 1 Reduced by water and sodium amalgam to succinic acid Zinc added to an aqueous solution of maleïc acid yields zinc maleate and succinate -2 Calcium maleate fermented in contact with cheese also changes to succinate (Dessaignes) —3 Electrolysis gives acetylene, succinic acid, and a small quantity of fumaric acid (Kekulé, A 130, 1) -4 Combines readily with bromine in the cold, forming iso dibromo succinic acid and some di bromo succinic acid derived from fumaric acid into which a portion of the maleic acid is at the same time transformed (Kekulé, Petri, A 195,59) Chlorine gives a di chloro succinic acid (Petrieff, Bl [2] 41, 309) Bromine in presence of water forms 180 di-bromo-succinie, bromo fumaric, bromo succinic, and fumaric acids (Wislicenus, A 246, 53) -5 Dissolves easily in aqueous HBr, the solution even at 0° soon depositing fumaric acid and bromo succinic acid in equimolecular proportions The bromo succinic acid may easily be extracted from the product by water (Fittig a Dorn, B 9, 1191)—6 Converted into fumaric acid by boiling cone HIAq, HBrAq, dilute HNO₃, or HClAq (Kekulé, A Suppl 1, 184, 2, 93, Kekulé a Strecker, A 223, 186) When HIAq is used the ultimate product is successed. succinic acid Dry HCl does not convert maleic acid into fumaric Maleic acid is converted into fumaric acid by heating its aqueous solution at 100°-180° (Semenoff, Bl [2] 46, 816) An aqueous solution of sodium maleate is not affected by being heated for 10 hours in a sealed tube at 100° to 185° -7 With hypochlorous acid it forms a compound which reduced by sodium amalgam yields inactive malic acid, oxymaleic acid (?), and a liquid which breaks up on heating into CO2 and $C_6H_{10}O_8$ (Petrieff) —8 KMnO₄ oxidises it to in active tartaric acid —9 Alcoholic NH₃ at 150° slowly forms aspartic acid (Engel, C R 104, 1805) —10 The acids of the maleic series readily split off H.O from their acid aniline salts, when the aqueous solution of the latter is left to stand for several days or boiled, a crystalline pp being formed of the acid anilide X" CO.HPh

an isomeride thereof Under the same conditions the acid aniline salts of the acids of the fumaric series are quite stable. This constitutes a ready method of determining to which of the two isomeric series a given acid belongs. The acid is half neutralised with aniline and either left to stand or heated to boiling, if a pp. s obtained insoluble in dilute HCl the acid belongs to the malric series (Michael, B 19, 1872).

Salts—KA" (dried at 100°). Radiating

Salts — K.A. (dried at 100°). Radiating crystals, v sol water, insol alcohol — KHA" aq small crystals, v sol water The solution reddens litmus.—Na.A". needles Ppd as a

granular crystalline powder by adding alcohol to its aqueous solution. Is not deliquescent—
NaHA" 3aq Triclinic crystals (Bodewig, J. 1881,
716) Sl sol cold water—KNaA" aq deliques cent crystalline powder (Büchner, A. 49, 60)—
BaA" 2aq gelatinous pp, changing to scales 8 11 at 20° (Regnault)—BaA"aq (Anschütz)—
BaH₂A", 5aq indistruct crystals, which redden litmus, v sol water (Büchner)—CaA"aq (dried at 100°) small needles, sol water—CaH₂A", 5aq long prisms, v sol water, insol alcohol—SrA"5aq silky needles—SrH₂A", 8aq rect angular prisms—MgA' 3aq—MgH₂A", 6aq hard crystals, v sol water, insol alcohol—ZnA" 2aq crystals, v sol water, insol alcohol—NiA"aq apple green crystals—CuA" light blue crystals, sl sol boiling water, v sol NH₂Aq, forming a solution whence alcohol ppts an azure blue crystalline powder—rbA" 3aq amorphous pp, changing to needles—Pb₂A"O (dried at 100°), Otto, A. 127, 178)—Ag,A' white pp, changing to lustrous needles—AgHA" (dried at 100°) needles

Acid aniline salt C₆H₅NH₃HA" jaq prisms, sol water On allowing the solution to stand for some days it forms phenyl aspartic acid C₆H₅NH C₂H₃(CO₅H₂ [132°] (Anschutz a Wirtz, A 239, 140, cf Michael, B 19, 1373, Am 9, .83, 197)—The neutral aniline maleate when boiled in aqueous solution de posits the phenylimide of phenyl aspartic acid C₆H₅NH C₂H₃ CO NC₆H₅, a body [212°] which was formerly described as the di anilide of maleic acid C₂H₂(CONHPh)₂

Phenyl-ımıde C₂H₂ CO NC₈H₈ [91°] (162° at 12 mm) Formed by the dry distilla tion of acid aniline malate (Anschutz a Wirtz, Am 9, 238, cf Michael a Wing, Am 7, 280) Long yellow needles, v sol benzene, CHCl, ether, and alcohol, sl sol CS₂ and ligroin Its solution in chloroform takes up bromine, forming the phenyl imide of di bromo succinic acid [159°] Baryta water at 40° gives the acid anilide of fumaric acid

Mono methyl ether HMeA" Probably exists in the solution of maleic anhydride in MeOH Such a solution becomes hot when mixed with NaOMe, probably forming NaMeA", but the solution presently deposits a bulky white, partly crystalline, pp, which forms an alkaline aqueous solution, becoming neutral on boiling, the neutral solution contains the methyl derivative of sodium methyl malate

C₂H₂(OMe)(CO₂Na)(CO₂Me) (Purdie, C J 47, 873)

Di methyl ether Me,A" (205° 1V) S.G. 14 1 158 H.C. 669,570 (Ossipoff, C. R. 109, 812) From silver maleate and MeI, excess of iodine being avoided, as this would convert it into di methyl fumarate (Ansohutz, B. 12, 2282) Bromine effects the same change

Mono-ethyl ether HEtA" From the anhydride and boiling alcohol Also from HAgA' and EtI (Ossipoff, J R 20, 254) Not identical with the mono ethyl ether of fumaric acid Forms a salt NaEtA" By treating HEtA" with NaOEt and boiling the product with water C_.H₂(OEt)(CO_.Et)(CO_.Na) is obtained, identical with that derived from fumaric acid (Purdie)

Diethyl ether Ei,A" (225° 1 V) From Ag,A" and Etl (Ansohutz, B 11, 1644, 12, 2281) Vapour density corresponds to the formula (O) Colourless liquid Converted by iodine into the fumaric ether Bromine gives di bromo succinic ether Boiling with NaOMe forms a product whence boiling water produces $C_2H_4(OMe)(CO_2Et)_2$ (Purdig, C J 47, 868)

Di-isopropyl ether Pr₂A" Vapour density corresponds to the formula

CH CO Anhydride C,H2O, ve [53°] CH CO

(Anschutz), [57°] (Pelouze, A Ch [2] 56, 72), [60°] (Fittig, A 188, 87) (202° 1 V) (A) V D 48 (H=1) (calc 49) (Hubner a Schreiber, Z [2] 7, 712) HC 336,920 (Ossipoff, C R 109, Appears to be the sole anhydride of both maleic and fumeric acids

Formation —1 By rapidly distilling maleic or fumaric acid, and frequently rectifying the pro duct (Pelouze, A 11, 263, Kekulé, A Suppl 2, In vacuo, maleïc acid splits up into water and anhydride even at 100° (Reicher, R T C 2, 312) -2 By heating fumaric acid with AcCl and HOAc at 100° -3 From silver fumarate and fumaryl chloride (Perkin, B 14, 2545) -4 By distilling chloro or bromo succinic anhydride (Anschutz a Bennert, B 15, 643) - \$5 By dis tilling malic anhydride

Preparation -1 Malic acid is treated with an excess of acetyl chloride, and the product (which probably chiefly consists of acetyl malic anhydride) is distilled, when it splits up into acetic acid and maleic anhydride, the yield is 45 pc (Perkin, C J 39, 562, B 14, 2547) — 2 By dry distillation of malic acid and treatment of the residue and distillate with AcCl, the yield is 56 pc of the theoretical (Anschutz, B 12, 2281)

Properties — Trimetric crystals, a b c = 6408 1 4807 (Bodewig, B 14, 2788) In contact with water it is converted into maleic acid, which is conveniently prepared in this way The abnormal rapidity of the etherification of maleic acid by heating with alcohols appears to be due to an intermediate formation of anhydride (Reicher, R T C 2, 308) Maleïc anhydride heated in a sealed tube at 260° gives a carbonaceous residue and gases (Semenoff, Bl [2] 46, 816)

Reactions -1 Unites with bromine at 100°, forming iso-di bromo succinic anhydride, which is resolved at 180° into HBr and bromo maleic anhydride —2 PCl₂ gives the chloride of fumaric acid (Perkin, B 14, 2548), but maleyl chloride (71° at 11 mm) appears to be first formed (Anschutz a Wirtz) -3 With a saturated solution of HCl in HOAc it forms at 100° chlorosuccinic acid -4 When heated with phenylhydrasine (1 mol) at 150° it forms the phenyl hydrazide C.H. C.O. N.HPh, which crystallises in needles [259°], and turns brown at 180° (Hötte, J pr [2] 35, 295)—5 When heated with phenois it produces therescent compounds analogous to the phthaleins, which may therefore be called 'maleins'. The resorcin malein has a green fluorescence, (a) naphthol malein has a greenish-red fluorescence (Burckhardt, B 18, 2864)

Constitution -The constitution of fumaric

and maleic acids is discussed under Fumario ACID, vol 11 p 585 The anomalous formula CO₂H C CH₂ CO₂H for male c acid, based on the formula CO₂H CBr, CH₂ CO₂H, 1s rendered improbable by the observation that bromofumaric and not pyruvic acid is the product formed, together with CO₂, when baruum iso-di bromo succinate is treated with moist Ag₂O in the dark (Demuth a V Meyer, B 21, 264) Racemic acid is formed when silver iso di bromo succinate is boiled with water The representation of maleic and fumaric acids by formulæ in space has been discussed by Wisli cenus in his treatise Ueber die raumliche Anordnung der Atome in organischen Moleculen

References - Amido, Bromo, and Chloro MALKIC ACIDS

Allo maleïc acid v Fumaric acid MALEO-FLUORESCEIN C1.H12O. 6.6 C₂H₂(OH)₂ Obtained by heating resorcin

C₂H₂ CO

with maleic anhydride (Lunge a Burckhardt, B 17, 1598) Small needles Sol alcohol, sl sol water Dissolves in alkalis to a red solution, with a strong green fluorescence With KOH, MeI, and MeOH it gives a dimethyl derivative, C16H10Me2O6, crystallising in red needles AcCl in HOAc gives C16H10Ac2O6, crystallising from HOAc in yellowish needles, insol water, CHCl,

and benzene, sl sol alcohol (Burckhardt, B 18, 2864) MALEYL CHLORIDE v Chloride of Fumario

MALIC ACID C.H.O., 10
CO.H CH. CH(OH) CO.H Mol w 134 [100°]
S G 2 1 56 (Schröder, B 12, 1611) S G of solution -3148 Heat of neutralisation 24,919 (Gal a Werner, Bl [2] 46, 803) [a]_D = -3 in dilute solutions, as the liquid becomes more concen trated it approaches + 59

Occurrence - Malic acid was discovered by Scheele in 1785, but its composition was first correctly determined by Liebig (A 26, 166) It is very widely diffused in the vegetable king dom, being contained in plants sometimes in the free state, sometimes in the form of potassium. calcium, or magnesium salt. It is found in abundance, together with citric acid, in unripe apples, in the fruits of the barberry, sloe, elder, and mountain ash, and in gooseberries, cherries. bilberries, strawberries, raspberries, and many other fruits It is likewise found in the roots of marsh mallow, angelica, aristolochia, bryony, liquorice, primrose, and madder, in carrots and potatoes, in the leaves and stems of aconite, belladonna, hemp, celandine, holy thistle, lettuce, tobacco, poppy, rue, sage, house-leek, tansy, thyme, valerian, and melliot, in the flowers of chamomile, elder, and mullein, in pine apples and grapes, in the seeds of carraway, cumin, parsley, anise, flax, and pepper, in asafeetida, opoponax, and myrrh It also occurs in the leaves of the common ash (Gintl, Z [2] 5, 377), and in the fruit of the sumach (Reinsch, Z 1866, 221) Yolk, the sweat of sheep, contains potassium malate to the extent of 25 pc. of the solid residue (Buisine, C R 106, 1426).

Formation —1. Malic soid, with the same

optical properties as those with which it exists in plants, may be formed from asparagine or active aspartic acid by treatment with nitrous acid (Piria, A Oh [3] 22, 160) —2 Malio acid, with a rotatory power equal and opposite to that contained in plants, may be obtained from ordinary tartaric acid by the action of phosphorus, indine, and water (Dessaignes, A 117, 134, Bremer, Bl [2] 25, 6, B 8, 861, 1594)

Preparation —1 The juice of mountain-ash

berries, not quite ripe, after being pressed, boiled up, and filtered, is partly neutralised with carbonate of potassium, leaving, however, a suffi-cient excess of acid to redden litmus pretty strongly, then precipitated by nitrate of lead, set aside for a few days, till the curdy precipitate is completely converted into small needles, these crystals freed from the admixed mucous or flocculent compound of lead oxide and colour ing matter by careful elutriation with cold water, are, lastly, well washed with water The needles of impure malate of lead are boiled with a slight excess of dilute sulphuric acid, the filtrate divided into two equal portions, one portion exactly neutralised with ammonia, the other por tion then added, and the reddish liquid evaporated and cooled, it then yields nearly colourless crystals of acid malate of ammonia, which may be rendered quite colourless by recrystallisation These crystals are then precipitated by acetate of lead, and the precipitate, after thorough washing, is decomposed by sulphydric or sulphuric acid (Liebig) —2 The juice is boiled for some time with milk of lime in quantity not quite sufficient for neutralisation, and the pp poured into a boiling mixture of HNO₃ (1 pt) and water (10 pts) The acid calcium malate which crystallises out on cooling is recrystallised from water, dissolved in water, ppd by lead acetate, and the lead malate decomposed by H2S (Liebig, A 38, 259) By similar processes malic acid may be obtained from house leek, from cherries or barberries, from the berries of Rhus coriaria, from the stems of rhubarb, from apples, and from tobacco

Properties -The aqueous solution, concen trated to a syrup and left to evaporate in a warm place, yields groups of colourless shining needles or prisms of 4 or 6 faces They melt at 83° (Pelouze) or 100° (Pasteur), and do not suffer any loss of weight at 120° They deliquesce in the air, and are v e sol water and alcohol Dilute solutions of malic acid are lævorotatory, but the rotation changes so rapidly with concentration that concentrated solutions are dextro-These dextrorotatory solutions are rotatory rendered laworotatory by the addition of H2SO4 or of HOAc $[a]_{D} = 5.891 - 0.895q$ (where q = percentage of water in solution) (Schneider, A 207, Solutions of sodium malate containing about 54 pts of the salt to 46 pts of water are inactive at 20°, stronger solutions are lævorotatory, while more dilute solutions are dextrorotatory (Thomsen, J pr [2] 35, 153) soid kills algo (Zygnemaceæ) (Loew a Bokorny, J pr [2] 36, 272) Malic acid prevents the ppn. of cupric and ferric salts by alkalis, 2 mols holding 1 mol of CuO in solution (Hofmeister, A 189, 27, of Juette, Fr 7, 489) A dilute to-lution of malic acid or of a malate is not immediately ppd. by lime water or by CaCl, either in

the cold or on heating, but on the addition of alcohol a white pp of calcium malate separates (Braconnot, A Ch [2] 51, 331, H Rose, P 31, However, a solution of malic acid (1 mol) mixed with pure milk of lime (2 mols) may solidify to a pasty mass (Iwig a Hecht, A 238, A concentrated solution of an alkaline 171) malate is ppd by CaCl₂, but presence of NH,Cl hinders the ppn, which, however, takes place on adding alcohol Lead acetate gives a white pp, soluble in excess of malic acid and in ammonia, when the pp is heated in the mother liquid it melts to a semifluid translucent mass are not blackened by heating with fuming H,SO, Dilute HOAc at 60° dissolves lead malate, but not lead tartrate or citrate (Hartsen, Fr 14, 373, Ar Ph [3] 6, 110) Malic acid may be separated from oxalic and tartaric acids by ppg the latter with CaCl2, filtering, and ppg calcium malate by adding alcohol to the filtrate (Barfoed, Fr 7, 403) Ammonium malate may be separated from ammonium citrate, tartrate, and oxalate by solution in alcohol (Barfoed)

Reactions -1 Heated for some hours at 140° it yields water and fumaric acid it gives off water and maleic anhydride, while fumaric acid remains as a solid residue If the malic acid be suddenly heated to 200° and kept at that temperature a comparatively large quan tity of maleic anhydride is obtained The ma leic anhydride, combining with the water in the distillate, is partially converted into maleic acid Malic acid is carbonised when suddenly exposed to a red heat -2 By treatment with potash and bromine, bromoform is obtained (Cahours, A Ch. [3] 19, 507) -3 Nitric acid easily oxidises it to oxalic acid and CO2-4 Cone HIAq at 180° reduces it to succinic acid (Schmitt, A 114, 106) Succinic acid is also formed when calcium ma late is fermented in contact with yeast (Piria, A 70, 102, Liebig, A 70, 104, 363) Fermentation of calcium malate by certain Schizomycetes produces succinic, acetic, butyric, and propionic acids and ethyl alcohol (Fitz, B 11, 1896, 12, 481, cf Dessaignes, C R 28, 16, Liebig, A 70, 104, 363, Kohl, A 78, 252, Baer, Ar Ph [2] 69, 147, Winckler, Jahrb pr Pharm 22, 300, Rebling, Ar Ph [2] 67, 300, Béchamp, C R 70, 999) -5 By slow oxidation in the cold with K₂Cr₂O₇ it is converted into malonic acid (Des saignes, A 107, 251) -6 When boiled in dilute aqueous solution with MnO2 it yields a distillate containing aldehyde (Liebig, A 113, 14) -7 Heated with KOH it yields acetic and oxalic acid -8 When calcium malate (1 pt) is heated with PCl_s (4 pts) the chloride of fumaric acid passes over (Perkin a Duppa, A 112, 24, Lies Bodart, A 100, 327) —9 Boiling aqueous H₂SO at 135° gives aldehyde, CO₂, water, and CO (Weith, B 10, 1744)—10 The electrolysis of potassium malate gives aldehyde, CO2, and some acetic acid (Bourgoin, Bl [2] 9, 427) —11 Water containing a few drops of H₂SO, at 160° gives fumaric acid (Markownikoff, A 182, 351) — 12 When heated with phenol and H2SO, it gives

CO and C₀H, O-CO | (Pechmann, B 17, 929,

1649) —18 Long boiling with cone HClAq gives fumaric acid —14 Cone HBr at 100° gives brome-succinic acid and fumaric acid (Kekulé,

A. 180, 11) -15 Chloral at 125° forms | O CH CH₂ CO₂H | CCl₂ CH | [140°] This forms |

targe crystals, sl sol cold water (Wallach, A. 193, 42) With PCl₃ it gives the oily chloride C₂H₄Cl₄O₄, whence alcohol forms C₃H₄Cl₄(OEt)O₄ [46°], and MeOH gives C₂H₄Cl₃(OMe)O₄ [85°] — 16 Phenyl hydrazine at 120° forms C₁₃H₁₈N₁O₃ e C₂H₄O(CO N₂H₂Ph)₂ [223°], which crystallises from dilute alcohol in plates (Bulow, A. 236, 195, cf Fischer a Passmore, B. 22, 2734) — 17 Malic acid (3 p.s.) heated with mamidobenzoic acid at 150° forms a product whence by washing with hot water and alcohol, dissolving in aqueous NH₃ and ppg by HCl₃ there is obtained a white powder C₂H₄O(CO NH C₃H₄ CO₂H)₂. The ammonium salt of this acid forms with cupric acetate a pp of Cu₁(C₁₃H₁₃N₂O₇)₂. Ac₂O decomposes it, forming NHAC C₃H₄ CO₂H (Schiff, G. 16, 28, A. 232, 166)

Salts - Malic acid has a tendency to form At 200° the salts give off water and acid salts are converted into fumarates -NH4HA" trans parent trimetric prisms Not hemihedral, but becomes so after fusion and recrystallisation SG 125 1 55 +S 32 at 15 7° $[a] = -6^{\circ}$ dry distillation it forms fumarimide, fumaric, and maleic acids, and active and inactive malic acid Combines with acid ammonium tartrate Normal ammonium malate (NH₄)₂A" is v e sol water, and its solution gives off NH, to the air, becoming acid In a solution containing 63 p c of the salt $[a]_D = -42$ In a 17 p c so lution $[a]_D = -72$ (Schneider, A 207, 276)—

RHA" crystals Begins to decompose at 100° Sol water, insol alcohol $[a]_D = -5$ in a 21 p c solution, = -57 in a 94 pc solution at 20° K A" Uncrystallisable and deliquescent mass $[\alpha]_D = -22$ in a 62 pc solution, = -68 in a 94 pc solution at 20° (Schneider) —NaHA" Crystallisable and permanent in the air, sol water, insol alcohol $[a]_{D} = +0.15$ in a 60 6 p c solution, = -5 64 in a 20 pc solution at 20° (Schneider) — Na₂A" Uncrystallisable Uncrystallisable $[a]_{D} = +4.7$ in a 65.5 p c solution, = -8.4 in a 53 pc solution - *LiHA" Uncrystallisable $[a]_{p} = -4.6 \text{ in a } 50 \text{ pc solution}, = -8.4 \text{ in a}$ 10 pc solution - Li2A" Uncrystallisable $[a]_{D} = -41$ in a 39 pc solution, = -12 in a 6 pc solution at 20° (Schneider, A 207, 273) — BaA''aq thin plates $[a]_b = +82$ in a 9 4 p c solution, = -26 in a 2 p c solution at 20° — *BaH,A''₂ Uncrystallisable and more soluble than the neutral salt — SrA"aq (dried at 100°) Crystalline mass, v sol water — *SrH₂A" Crystalline pp formed by adding malic acid to a sotution of the preceding Sl sol cold, m sol hot, water—CaA" 3aq S 839 at 15°, 711 at 45°, 566 at 58°, 600 at 65°, 663 at 72°, 737 at 86° (Iwig a Hecht, A 233, 170) Granular crystalline mass When a solution of malio acid is added to lime water a pasty mass of A"Ca2(OH)29aq(?) is first formed, but when the theoretical quantity of malic acid has been added this dissolves up again, and the clear liquid deposits nodules of CaA" 3aq in the course of 24 hours —CaH₂A", 6aq (Hagen, A 38, 263) Occurs in stems of Geranium zonale, the berries of Rhus glabrum (Rogers, Am S 27, 294), and in tobacco Separates in well formed trimetric

octahedra from a solution of the neutral salt in warm dilute nitric acid S (of CaH₂A"₂) 1 287 at 15°, 8514 at 45°, 32 236 at 57°, 13 127 at 68°, 7437 at 78° (I a H) $[a]_D = +5$ (Bremer, R T C 3, 164) When the solution obtained by neutralising malic acid with CaCO, is boiled a nearly insoluble granular pp is got, which consists of CaA"aq (Richardson a Meundorf, A 26, 135), or of CaA" (Hagen, A 38, 257) — MgA" 5aq Prisms, which separate from a highly concentrated solution (Liebig, A 5, 148) Alcoholppts MgA" -MgH2A"24aq (or 3aq) Flattened prisms - ZnA"3aq Monoclinic crystals (Handl, J 1859, 289) Slowly deposited in the cold from the product of solution of zinc carbonate in aqueous malic acid at 30° When these substances are boiled together a basic salt ZnO(ZnA")2 4aq is deposited as a jelly, changing to a sandy powder, while the filtrate deposits ZnA" 3aq as hard, four sided prisms S 17at 20° — ZnH₂A"₂ 2aq Elongated octahedra S 4 in the cold — The neutral manganese salt is very soluble and uncrystallisable, by adding malic acid to its solution the acid salt is ppd as a white powder, S 25 From boiling water it separates in rose coloured crystals -The neutral and acid ferric salts are gummy masses. sol water and alcohol - CuA" aq gummy mass, v sol water —CuH₂A"₂2aq blucrystals, obtained by evaporation at 40°-CuO(CuA"), 4aq green insoluble powder obtained by boiling aqueous malic acid with cupric If evaporated at 45° dark green carbonate crystals of CuO(CuA"), 6aq may be got H Schulze (Ar Ph [2] 57, 273) obtained green crystals of a double salt of cupric malate and ammonium sulphate -PbA"3aq Obtained by ppg neutral lead acetate with a solution of calcium or potassium malate, as a white curdy pp which slowly changes to radiating four sided needles Melts in boiling water V sl sol cold, m sol boiling, water, from which it is deposited in needles Dissolves easily in nitric acid, acetic and malic acids do not dissolve it more readily than water When dry it does not melt at 170° but at 220° it forms lead fumarate—PbA" aq (dried at 100°) (Otto, A 127, 175) — PbO(PbA')... Obtained by digesting the neutral salt with am monia, or by dropping a solution of a neutral malate into a boiling solution of lead subacetate Amorphous pp, not becoming crystalline Does not melt under water Melts under hot dilute HOAc, evidently changing to the neutral salt Nearly insol water, to which, however, it imparts an alkaline reaction—AgoA" White parts an alkaline reaction —Ag₂A" White granular pp, formed by adding silver nitrate to a solution of neutral or acid ammonium malate Anılıne malate C.H.,NH,HA" [144°] White prisms (from alcohol) On dry distilla tion it gives water, aniline, the phenyl imide of phenyl aspartic acid [211°], and the phenylimide of maleic acid [91°] (Anschutz a Wirtz, Am 9, 237, A 239, 140)
Acetyl derivative CH, (OAc) (CO₂H),

Acetyl derivative CH₃(OAc)(CO₂H)₂ [132] From the acetyl derivative of the an hydride and water (Anschutz, A 254, 165) Dr-methylether Me₂A" (1223 at 10 mm)

by passing HCl into a cooled solution of malic acid in MeOH (Demondesir, A 80, 301; C. R

23, 227, Anschütz, B 14, 2790, 18, 1953) — Ca(MeA"), 18 sol alcohol

Acetyl derivative of the di methyl

ether CaH₂(OAc)(CO₂Me), (129° at 11 mm)

From the ether and AcCl

De-ethyl ether Et.A" (128° at 10 mm) Formed in like manner Can only be distilled en vacuo -Ca(EtA"), is sol alcohol

Acetylderivative of the di ethylether

C₂H₃(OAc)(CO₂Et)₂ (187° at 12 mm)

Nitroxyl derivative of the di-ethyl

ether C₂H₃(ONO₂)(CO₂Et)₂ S G ¹² 1 202 From the ether, fuming HNOs, and conc H, SO, (Henry,

B 3, 532) Thick oil

Din . n . propyl ether C.H. (OH)(CO.Pr). (151° at 10 mm) (Anschutz)

Acetyl derivative of the di-n propyl ether C₂H₂(OAc)(CO₂Pr)₂ (157° at 12 mm)

Mono isoamyl ether

C₂H₃(OH)(CO₂H)(CO₂C₅H₁₁) From malic acid
and isoamyl alcohol at 120° (Breunlin, A 91,
323)—NH₄A' needles—CaA'₂aq plates

Acetyl derivative of the anhydride CH(OAc) CO [54°] (161° at 14 mm)

CH,-Formed, together with maleic anhydride, by heating malic acid with AcCl (Anschutz, B 14, 2791) Decomposed by distillation under atmospheric pressure into HOAc and maleic anhydride

 $C_2H_3(OH)(CONH_2)_2$ Amide Malamide When gaseous NH, is passed into an alcoholic solution of malic ether crystals of malamide are deposited Separates from water in well defined Resolved by hydrolysis into NH, and crystals malic acid

Amicether $C_2H_3(OH)(CO_2Et)(CONH_2)$ Malamic ether Formed as a crystalline mass when gaseous NH, is passed into malic ether (Pasteur, J 1853, 411)

Dr-antlide C.H. (OH)(CONHPh), [175°] Formed, together with the phenylimide, by boiling aniline (2 mols) with malic acid (1) The phenyl imide is extracted by boilmols) ing water, and the residue recrystallised from alcohol, using animal charcoal (Arppe, A 96, Colourless scales Nearly insol water. dilute acids, and alkalis

Mono anrivac C₂H₃(OH)(CO₂H)(CONHPh) Malanthe acrd [145°] Obtained by boiling the phenyl-imide with aqueous ammonia, the product is ppd by baryta, and the Ba salt de composed by H.SO., avoiding any excess White granules composed of very minute needles (from alcohol), v sol water, m sol alcohol, sl sol ether Reddens litmus Hot dilute H,SO, re solves it into water and the phenyl imide white pp, salts are soluble in water -AgA' erystallising from water in shining scales

Phenyl - 1mide C2H3(OH) CONPh. [170°] Formed by heating malic acid with aniline and crystallising from water Groups of delicate needles, v sol water, alcohol, and ether

Inactive malic acid CO_H CH_ CH_(OH) CO_H [c 108°] (Pictet, B 14, 2648), [c 114°] (Kekulé), [183°] (Pasteur, Loydl, Bischoff) Occurs as calcium salt in the leaves of the common ash (Fraxinus ex-ectsion) (Gintl, J 1868, 800, Garot, J 1853, 409)

Formation -1 By mixing equal parts of levo- and dextro main acids (Van't Hoff, jun, B 18, 2170, R T C 4, 130) -2 By reducing racemic acid with HIAq (Bremer, Bl [2] 25,6) — 8 By the action of nitrous acid on inactive aspartic acid obtained from fumarimide (Pasteur, A Ch [3] 34, 46, A 82, 330) -4 By the action of moist Ag.C on bromo succinic acid (Kekulé, A 117,126, 130, 24) -5 By heating fumaric soid with a large quantity of water at $150^{\circ}-200^{\circ}$ (Jungfleisch, Bl [2] 30, 147) -6 By heating fumaric acid (1 pt) with NaOH (4 pts) and water (40 pts) for 100 nours at 100 (Linne mann a Loydl, A 192, 80, B 9, 925) —7 To gether with fumaric acid, by treating di \$\beta\$ chloro propionic ether with a weak alcoholic solution of KCy, and boiling the product with potash (Werigo a Tanatar, A 174, 367) Also in like manner from di & bromo propionicacid (Tanatar, B 13,160) —8 From chloro ethanetri carboxylic ether CO2Et CH2.CCl(CO2Et)2 and dilute alcoholic KOH (Bischoff, A 214, 49)

Properties - Crystallises more readily than active malic acid, being less soluble in water and not deliquescent, or at any rate less deliquescent than the active acid V e sol water, v sol alcohol, v sl sol ether When heated at 200° it yields fumaric acid

Salts -NH, HA" trimetric crystals (Van't Hoff) -NH, HA"aq monoclinic crystals a b c = $5856 \ 1 \ 5377$, $\beta = 68^{\circ} \ 12'$ —CaA" granular pp, sl sol water—CaA" aq—CaA" 2½ aq no dules of transparent crystals (Pasteur) The acid calcium salt resembles that of the active acid except that its crystals exhibit hemihedral faces The lead salt melts under water, but crystal lises less easily than the mactive salt. The lead salt obtained by Tanatar from di bromo propionic acid did not melt under water -Ag, A"

By crystallising the cinchonine salt Bremer (B 13, 352) was able to separate it into salts of

lævo and dextro malic acid

EthylderivativeC₂H₄(OEt)(CO₂H)₂. [86°] Obtained by saponifying its di ethyl ether (Purdie, C J 39, 348) Transparent crystals (from ether), sol water Not ppd by lead subacetate, but in neutral and feebly acid solution it is ppd by lead nitrate and, more slowly, by neutral lead acctate Fuming HI at 120° reduces it to succinic acid —CaA" insoluble —Ag₂A" sl sol water —BaA"aq hygroscopic, v sol water

Dr ethyl ether of the ethyl deriva tive O.H. (OEt) (CO.Et), (195°-200°) at 250 mm From fumaric ether and NaOEt, the product being neutralised (Purdie)

Isobutyl derivativeC,H,(OC,H,)(CO,H), Crystalline, deliquescent mass (Purdie) -CaA msol water -Ag,A" flocculent, insol water

The following compounds are probably also derivatives of the same inactive malic acid -

Amic acidCO₂H CH₂ CH(OH) CONH₃ [146°] Obtained, together Malamic acid with its ether, by boiling the amide of diazosuccinic ether with water (Curtius, J pr [2] 88, 479) Colourless prisms, v sol water, alcohol, and ether

Methyl ether of the amic acid CO.Me CH, CH(OH) CONH, [1056]. Formed, together with methyl fumaramate, by boiling water, forming di bromo barbituric acid Nitiis methyl diazo succinamate

CO2Me CH, CN, CONH,

with slightly acidified water (Curtius, J pr [2] 88, 482) Silky plates, v e sol alcohol, ether, and water With benzoic acid at 150 it forms crystalline CO2Me CH2 CH(OBz) CONH2 [80°], v sol ether

of the ethyl Benzoyl derivative ether of the amic acid CO,Et CH, CH(OBz) CONH, [97°] Formed by heating ethyl diazo succinamate with HOBz

Colourless hombohedra

Dextro-malic acid CO2H CH2 CH(OH) CO2H [c 100°] Formed from dextro asparagine (from sprouting vetch seeds) by treatment with nitrous acid (Piutti, B 19, 1693) The cinchonine salt is obtained by crystallisation from the cinchonine salt of mactive malic acid Resembles ordinary malic acid, except that it is dextrorotatory

Isomeride of malic acid C₄H₆O₅ [155°-168°] Formed by heating acetylene dibromide (5 pts) with KCy (4 pts) and alcohol (28 pts) at 100° and saponifying the resulting nitrile with potash (Sabanejeff, A 216, 275) Crystals, v sol water -Ag₂A"

Isomalic acid of Kammerer (J pr 88, 321 A 139, 257) is identical with citric acid (Ostwald, B 21, 3534)

Paramalic acid is described as Dictycollic

Iso-malic acid CH₃ C(OH)(CO₂H)₂ [c 140° From brome iso succinic acid and moist Ag.O (Schmoger, J pr [2] 14, 77, 19, 168, 24, 38) Crystals, v sol water, alcohol, and ether At In 170° it splits up into CO2 and lactic acid active Its neutral solutions give no pp with CaCl2 (unlike methyl tartionic acid, which gives a pp on warming) -BaA" 2aq amorphous pp S 1 at 100° Loses its water of crystallisation at 130° (unlike methyl tartionic acid) -PbA'

Does not melt under water —Ag,A" needles

Methyl-tartronic acid CH, C(OH)(CO H)2 Obtained from pyruvic acid by addition of KCy and HCl, the product being boiled with baryta water (Bottinger, B 14, 148, 17, 144) Rhombohedial crystals Decomposes on fusion, giving off CO Boiling conc HClAq splits it up into CO and lactic soid -BaA"aq (dried at 130°) Heavy crystalline powder, ppd on boiling — ZnA" 2aq crystalline powder —

Ag2A"aq white crystalline powder Reference -Bromo Malic acid

MALLOTOXIN C11H10O, or C18H16O, be extracted by CS, from finely-divided kamala, a yellow dye got from the seeds of Mallotus Phillipensis (A G Perkin a W H Perkin, jun, B 19, 8109) Flesh coloured needles, insol water, v sol hot alcohol Dissolves readily in alkalis, forming a yellowish red solution Ac.O yields a di acetyl derivative, r ROTTLERIN

MALOBIURIC ACID C.H.N.O. s.e

CO NH CO CH CO NH (?) Formed, as am monium salt, by heating barbituric acid (malonyl urea) with urea at 160° (Baeyer, A 135, 312) Formed also by boiling cyanuromalic acid with HClAq (Nencki, B 5, 888) Ppd by adding HCl to solutions of its salts as a granular pp which, when quite pure, can be obtained in crystals Dissolves completely in bromine and

acid converts it into nitro barbituric (dilituric) acid —KA'aq long needles S 16 in hot water MALONAMIC ACID v MALONIC ACID

MALONAMIDE v Amide of Malonic acid MALONANILIC ACID v Mono-analide of MALONIC ACID

MALONIC ACID C,H,O, ** e CH,(CO,H), Mol w 104 [134°] (Krafft a, Noerdlinger, B 22, 816) S 109 at 1°, 138 at 16° (Miczynski, 22, 816) \$ 109 at 1°, 138 at 16° (Miczynski, M 7, 258), 109 at 15° (Bourgoin, Bl [2] 33, 428) HF 212,700 (Stohmann, Kleber a Langbein, J pr [2] 40, 206) HC v 207,900 HC p 207,300 (S, K a L), 208,650 (Lougunine, C R 107,597) Heat of solution = -4573 Heat of neutralisation by NaOH 27,120 (Gal a Werner, Bl [2] 46, 803), 26,650 (Massol), by KOH 27,300, by NH, 25,040, by BaO₂H, 30,135, by CaO₂H₂ 27,090 (Massol, C R 107, 257, 393, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 108, 813, 10 1060, 109, 27) SH (0° to 50° 110°) 3262 (Hess, P [2] 35, 410) SH (0° to 50°) 2832, (0° to

Occurrence - In beet root (Lippmann, B 14, 1183)

Formation -1 Discovered by Dessaignes (C R 47, 76) as a product of the slow oxidation of malic acid by cold aqueous K2Cr2O, -2 By the action of alkalis or acids on cyano acetic acid (semi nitrile of malonic acid) or cyano acetic ether (Kolbe, A 131, 349, Hugo Muller, C J 17, 109) -3 By oxidation of allylene or propylene with cold alkaline KMnO, (Berthelot, J 1867, 335) -4 By boiling barbituric acid with potash (Baeyer, A 130, 143, Heintzel, A 139, 129) -5 By boiling mucobromic acid with baryta water (Jackson a Hill) -6 From di chloro acrylic ethei by treatment with Ag,O at 125°, and saponifying the product (Wallach a Hunaeus, A 193, 25) -7 By treating CBr, CO CH, CBr, with fuming HNO, (Demole, B 11, 1714)

Preparation -1 From ethylic, or better from

Chloro acetic acid potassic, chloro acetate (100 g) dissolved in water (200 g) is neutralised by K₂CO₃ (75 g), mixed with KCy (70 g), and warmed The reaction heats the liquid to boil KOH (100g) is now ing and is soon over added, and the liquid boiled as long as NH, escapes The liquid is then acidified with HCl, evaporated to dryness, and the malonic acid ex tracted by ether (H v Miller, J pr [2] 19, 326, cf hinkelstein, A 133, 338) —2 Chloro acetic acid (100 pts) is dissolved in twice its weight of water, and neutralised with potassium carbonate (75 pts) To the solution is added 75 to 80 pts potassium cyanide (98 pc), and the mixture heated for two hours, with continual renewal of the evaporated water The remaining mass is decomposed with concentrated potash When the odour of ammonia has disappeared the solution is neutralised with hydrochloric acid, and ppd as a calcium salt. This is decomposed with the requisite quantity of oxalic acid, the residue extracted with ether, and the solution evaporated (Conrad, A 204, 121) -3 By dissolving chloro acetic acid (100 gms) in double its weight of water, saturating the solution with potassium bicarbonate (110 gms), adding potassium cyanide (75 gms), and warming on the water bath At the end of the reaction double the volume of odnoentrated hydrochloric acid is added and the precipitation of potassium chloride rendered com plete by passing in a current of HCl gas The potassium and ammonium chlorides are filtered off, and the filtrate evaporated The nearly dry residue is taken up with ether, which on evaporation yields pure malonic acid (70 gms) (Bourgoin, A Ch [5] 20, 271) —4 Chloro acetic ether is boiled with pure KCy dissolved in 70 pc alcohol for 4 hours The alcohol is distilled off, and the residue mixed with dilute HCl and evaporated to dryness The cyano acetic ether is extracted with ether and decomposed by fuming HClAq at 100° (Petrieff, J R 10, 64, B 7, 400) —5 In like manner from bromo acetic ether (Franchimont, B 7, 216)

Properties —Triclinic lamins or prisms De composes a little over its melting point into CO₂ and acetic acid, but when heated under 10 mm pressure it may be sublimed V sol water, alcohol, and ether When heated with Ac.O, ma lonic acid gives a reddish yellow liquid with greenish yellow fluorescence — 001 g is sufficient for this test (Kleemann, B 19, 2030) A small quantity of malonic acid treated with urea and POCl₃ yields a product which when evaporated with nitric acid leaves a residue which gives with ammonia the purple colour due to

murexide (Grimaux, C R 88, 85)

Reactions -1 A solution of the free acid is hardly affected by the passage of an electric cur rent But the electrolysis of a concentrated al kaline solution gives off oxygen, CO, and CO2 at the positive pole, without any hydrocarbon (von Miller, Bourgoin, A Ch [5] 20, 80, C R 90, 608)—2 Malonic acid (5g) heated with bromine (10 cc) and water (12 cc) for 18 hours at 120° to 145° gives bromoform, tri bromo acetic acid, CO_2 , and HBr (Bourgoin, Bl [2] 34, 215) -3 HNO₃ (S G 153) in the cold gives off CO_2 (2 mols) (Franchimont, R T C 3, 422) -4PCl, gives malonyl chloride and a compound C₈H₄ClO₆, crystallising in needles [122°], decom posed by water and alcohol with evolution of CO₂ (Behal a Augur, Bl [2] 50, 631) —5 Malonic acid (1pt), NaOAc (1pt), and Ac₂O (3pts) at 100° forms a brownish yellow acid CilH4Os The sodium salt C₁₁H₃NaO₈ is v sol water, alkalis, and cone H₂SO₄, m sol HOAc Its solu tions exhibit fluorescence, but on heating CO2 is evolved and the fluorescence disappears acetic acid solution of the salt C11H3NaOs boiled with a solution of phenyl hydrazine acetate forms CO₂, NaOAc, and C₁₀H₄O₄(N NHPh)₂, a substance insol water and ether, v sol alcohol and HOAc, forming a green solution in conc H₂SO₄, and melting with decomposition about 180° (Kleemann, B 19, 2030) -6 Benzoic alde hyde and HOAc forms benzylidene malonic acid C₂H, CH C(CO₂H)₂ —7 Propionic aldehyde and HOAc gives CH, CH, CH CH CO2H (Komnenos, 4 218, 168) -8 o Oxy benzoic aldehyde and HOAc at 100° forms coumarin-carboxylic acid (vol 11 p 269) —9 Cunnamic aldehyde and HOAc at 100° gives phenyl-butinene dicarboxylic acid C₆H₅ CH CH CH C(CO₂H)₂ (Stuart, C 49, 366) -10 Heated with phenyl throcarbimide it gives acetanilide and the dianilide of malonic soid (Moine, Ann Chim Farm [4] 4, 201)
Salts The salts, with the exception of

Salts—The salts, with the exception of those of the alkali metals, are sparingly soluble in water, more soluble in dilute malonic ackl, HOAc, or nitric acid (Finkelstein, A 133, 338)—NaHA" 4aq: well defined crystals (F.).—

NaHA" aq trimetric prisms (Shadwell, **J** 1881, 699) —Na A" aq (Mulder, Bl [2] 29, 532, cf Massol, C R 107, 393) —KHA" 3aq prisms — KHA" monoclinic prisms (Haushofer, J 1881, 699) -K2A"2aq deliquescent monoclinic crys Gives CO2 and hydrogen on electrolysis tals (H von Miller) —K₂A" aq monoclinic prisms (H)—NH₄HA" verx deliquescent crystals Heat of formation from solid malonic acid and NH, 22,780 (Massof, C R 108, 1060) — (NH,).A" very deliquescent needles Heat of formation from solid malonic acid and NH, 41,015 -BaA" 2aq bulky focculent pp gradu ally becoming crystalline Crystallises from water in long slender needles At 100° it loses aq, and when heated in a current of hydrogen at 140° it becomes anhydrous BaA" aq is not dehydrated by heating in air at 150° (Pinner a Bischoff, A 179, 84) S 14 at 0°, 20 at 18°, 32 at 70° (Miczynsky, M 7, 261) Heat of so--3830 (Massol, C R 109, 29) lution CaA"2aq monoclinic needles (from water)
Ppd in gelatinous form on adding CaCl₂ to a solution of ammonium malonate S 3 at 0°, 37 at 20° , 47 at 72° (Miczynski) According to Massol (C R 108, 813) this salt separates in small brilliant scales on slow evaporation of its solution at 35°—CaA" 4aq silky needles Obtained by sow evaporation at 15° (Massol) V sl sol water May be dehydrated in a current of hydrogen at 135°—SrA" small brilliant scales (Ossipoff, C R 108, 815)—MgA" 2aq, MgA" aq, and MgA" 2aq are described by Finkel stein as crystalline powders - ZnA" 2aq mono clinic crystals - MnA" 2aq trimetric prisms -CoA" 2aq monoclinic crystals (Haushofer) -NiA'2aq bluish green powder - CdA" quescent — CdA" 4aq monochnic crystals — CdA" 12aq triclinic (Haushofer, J. 1882, 362)
— PbA" crystalline powder — (1882, 362) CuA" 3aq blue triclinic crystals (H) —CuO\" bluish green pp —Ag,A" crystalline pp, not blackened by boiling water —Ethylamine salt NEtH3HA" gives at 180° water and the CH CO

ethylimide of fumaric acid # NEt,

whence concentrated caustic potash solution forms NHEt CO CH CH CO₂H [126°] (Piutti, C C 1888, 1529)

Methyl ether Me,A" (1815° cor) SG 15 11603, 25 11511 (Perkin, C J 45, 509), 5 11753 (W) M M 528 at 17° SV 1376 (Wiens, A 253, 297) From silver malonate and MeI (Osterland, B 7, 1286) Oil, sol alcohol and ether

Mono-ethylether CO₂Et CH₂ CO₂H When alcoholic KOH (1 mol) is added to alcoholic malonic ether the liquid forms a crystalline pulp of CO₂Et CH₂ CO₂K composed of needles (Van't Hoff, B 7, 1571, Freund, B 17, 780) PCl₃ converts it into CO₂Et CH₂ COCl (170°-180°)

Ethyl ether CH_(CO,Et), (198° cor) (Per kin, C J 45, 508), § 1 0761 (Wiens) SG ½ 1 0610, § 1 10625 M M 7 41 at 14° SH 439 at 0°, 45 between 10 6° and 82 2° (R Schiff, Zert Phys Chem 1, 376, G 16, 454) SV 185 1 (Wiens, A 253, 297)

Preparation.—1 Calcium malonate is bailed with H₂SO, and 4 times the theoretical quantity of alcohol for 24 hours (Conrad, B 12, 749)—

2 Chloro acetic acid (250 g) is dissolved in water (500 g) and K,CO, (187 g), KCy (175 g) is added, and the whole heated on a sand bath until the reaction begins. The product is evaporated until its temperature is 135° , and is then allowed to cool. When cold it is treated with two-thirds of its weight of alcohol and gaseous HCl is passed in. The product is poured into iced water, extracted with ether, dried over CaCl₂, and distilled (Venable a Claisen, A 248, 131). Tricarballylic ether (287°) is obtained as a by product (Dau michen, C C 1888, 1347).

Reactions —1 Water at 150° gives CO, and acetic ether (Hjelt, B 13, 1949) —2 Boiling with m amido benzoic acid and a little alcohol forms CH2(CO NH C6H4 CO2H)2, a powder which will not melt and is insol water, hardly sol boiling alcohol, sol dilute NH, Aq, and dissolves without change in conc H,SO, (Schiff, A 232, 143, B 17, 403, G 15, 534) The intermediate com-17, 403, G 15, 534) The intermediate compound CO₂Et CH₂ CO NH C₆H₄ CO₂H [173°] is also formed at the same time -3 Chlorine forms chloro malonic ether -4 Cautious treatment with nitric acid (5 pts of S G 15) gives nitro malonic ether (Franchimont a Klobbie, R T C 8, 283) -5 According to Lang (B 19, 2937) zinc methyl or zinc ethyl act in the cold, forming phloroglucin tricarboxylic ether, methane, and ethane -6 When a mixture of malonic ether (1 mol) and LtI (2 mols) is heated with zinc there is formed ethane and ethyl-malonic ether (90 pc of the theoretical amount) (Daimler, B 20, 203) When malonic ether (20 g), EtI (100 g), and granulated zinc are heated with inverted condenser at 100° there is formed di ethyl malonic ether (Joulowsky, J pr [2] 39, 446) 7 With allyl rodide and zinc there is formed di-allyl malonic ether and propylene (Matvéeff, J pr 39, 452) - 8 When malonic ether (2 mols) is treated with glyoxal (1 mol) and zinc chlor ide it forms di oxy butane tetracarboxylic ether (CO₂Et)₂CH CH(OH) CH(OH) CH(CO₂Et)₃ (Polonowsky, A 246, 1) -9 With benzoic aldehyde and HCl it forms benzylidene malonic ether C.H. CH C(CO.Et) (Claisen a Cremer, A 218, 129)—10 Furfuraldehyde and acetic anhy dride give furfuryl methenyl malonic ether C4H3O CH C(CO2Lt)2 which boils with slight de composition at 293°, and gives on saponification the acid ether C,H,OCH C(CO,H)(CO,Et) [102 5°], and finally the acid C,H,O CH C(CO,H), [187°], which may be reduced by sodium amalgam to C₄H₃O CH₂ CH(CO₂H)₂ [125°] (Marckwald, B 21, 1081) -11 Aldehyde formsCH, CH C(CO.Et), and CH₃ CH₃(CH(CO₂Lt)₂)₂ (Komnenos, A 218, 145)—12 Diazobenzene chloride forms benzene azo malonic acid, identical with the phenyl hydrazide of mesoxalic acid (R Meyer, B 21, 118)

Sodium malonic ether CHNa(CO,Et)₂
Formed, with evolution of hydrogen, by dissolving sodium in malonic ether. The reaction is stopped by the crust of the sodium compound which forms on the surface of the metal, but this may be removed by adding alcohol (2 vols) which first forms NaOEt, and his then reacts with the malonic ether. The sodium malonic ether crystallises on cooling, and may be freed from alcohol by heating to 150° in a current of hydrogen (Conrad, B 12, 750). If, however, it be required merely for synthetical purposes the presence of alcohol is for the most part not injurious, and

the mixture of malonic ether and alcoholic NaOEt may be used at once This reacts upon organic halogen compounds thus —

CHNa(CO₂Et)₂ + XI = CHX(CO₂Et)₂ + NaI, the reaction being energetic at first but often requiring heat to finish it. If the substances are mixed in the right proportion the end of the reaction is recognised by the solution becoming neutral. Water is then added, and if X is a hydrocarbon radicle, CHX(CO₂Et)₂ separates as an oil, which may be purified by fractional distillation. The resulting CHX(CO₂Et)₂ still contains hydrogen displaceable by sodium, and if it be mixed with alcoholic NAOEt and another halogen compound say YI, the reaction

 $\begin{array}{c} \bar{C}NaX(C\bar{O}_2Et)_2 + Y\bar{I} = NaI + CXY(CO_2Et)_2 \\ takes place (Conrad a Bischoff, A 204, 121) \\ When the substituted malonic ethers are sapon fied acids are obtained, which at 150° or 160° give off <math>CO_2$ and leave derivatives of acetic acid $CHX(CO_2H)_2 = CO_2 + CH \times CO_2H \\ \end{array}$

 $CXY(CO_2H)_2 = CO_2 + CHXYCO_2H$ Hence malonic ether may be used, like aceto acetic ether, to effect the synthesis of organic acids of the general formula CXYH CO2H where X and Y may be alkyls, groups like CH₂ CO₂Et, or other radicles When it is desired to prepare a di alkyl malonic ether it is not necessary to perform the operation in two stages, for the proper quantity of NaOEt (2 mols) may be added all at once, and then the alkyl rodide (2 mols) By the action of AcCl on sodio malonic ether in ethereal solution it may be converted into acetylmalonic ether (120° at 17 mm), which is soluble in KOHAq, the yield is 55 pc of its weight. This ether forms an oxim and a phenyl hydrazide and therefore appears to be CH, CO CH(CO,Et)2. When sodio aceto-acetic ether is acted upon by chloroformic ether ClCO2Et the same ketonic ether CH, CO CH(CO₂Et)₂ should be formed, but the product is found to be insol conc KOHAq, and to boil at a higher temperature (127° at 17 mm) It is decomposed by cold dilute KOH, and gives CO₂ and alcohol The latter compound would therefore appear to be CH, C(OCO,Et) CH CO,Et (Michael, Am 10, 158, J pr [2] 37, 473, cf Lange, B 20, 1325

Reactions—1 EtI gives ethyl malonic ether 2 Bensyl chloride gives mono and di benzyl malonic ether and regenerated malonic ether Bischoff a Siebert, A 230, 94)—3 Malonic ether (32 g), sodium (9 2 g), dry alcohol (200 g) and chloroform (12 g) react thus (Conrad a Guthzeit, A 222, 250)—2CNa (CO_Et)₂ + CHCl, = 3NaCl+CNa(CO Et)₂ CH C(CO_Et)₂ torming sodium di carboxy glutaconic ether (q v)—4 Trimethylene bromide reacts with formation of

(CO_LEt)₂ CCCH₂ CH₂ (Perkin, jun, C J 51, 1, 702, 820)—5 NaOEt, allyl iodide, and iso butyl iodide gives an acid C₁₀H₁₄O₄ instead of allyl isobutyl-malonic acid—6 Chloro-formic ether ClCO₂Et forms methane tricarboxylic ether CH(CO₂Et)₃ (Conrad a Bischoff, A 214, 31, Claisen, B 21, 3567)—7 Tri bromo-denatro-bensene dissolved in ether reacts with formation of C₈H₂Br(NO₂)₃CH(CO₂Et)₂[75°], although bromo-benzene does not react (Jackson a Robinson, B 21, 2034)—8 Phthalyl chloride (1 mol) added to sodium-malonic ether (2 mols) dissolved in ether forms phthalyl malonic ether C₁₆H₁₄O₆

[75°], phthalyl-dimalonic ether $C_{22}H_{26}O_{10}$ [48 5°], and 'phthaloxyl dimalonic' ether (c_2H_{2i}) , 116 5°] (Wishcenus, A 242, 28) —9 Treatment with the chloride of mono-eth_il phthalate CO₂Et C₆H₄ COCl dissolved in benzene forms (CO,Et C,H, CO),C(CO,Et), [above 180°] (Zelinsky, B 20, 1012) —10 In alcoholic solution it is probably converted by carbonic acid gas into (CO,Et)₂CH CO₂Na (Michael, *J pr* [2] 35, 458) — 11 Carbon disulphide added to an alcoholic solution of sodium malonic ether gives yellow plates of (CO₂Et)₂CNa CS₁Na —12 SO₂ acts according to the equation SO₃ + CHNa(CO₂Et)₂ + HOEt = CH₂(CO₂Et)₂ + NaO SO OEt —18 Resorcin dissolved in alcoholic sodium malonic ether gives a greenish blue fluorescence, when after a few days the liquid is poured into water and acidified a small pp of needles of a condensation product $C_{11}H_0O_0$ [191°] is got A little above its melting point it is split up into CO2 and (β) methyl um belliferone of which it is probably the carboxylic acid (Michael, J pr [2] 37, 469) -14 Sulphur dissolves in alcoholic sodium-malonic ether, and at 100° crystals separate From these, acids liberate a stinking oil (thiotartronic ether?) -15 With alcohol and cinnamic ether at 100° The wind according to Containing the resulting acid, phenyl glutaric acid CO_H CH₂ CO₂H. The resulting acid, phenyl glutaric acid CO_H CH₂ CHPh CH₂ CO₂H. is got (Michael, J pr [2] 35, 349) -16 Phenyl cyanate PhNCO acts violently upon an alcoholic solution of sodium malonic ether with formation of (CO2Et)2CH CONHPh [124°] and the salt of an acid C₁₂H₂NO₂ [172°] (Michael, J pr [2] 35, 452) —17 Phenyl thio carbinide forms crystalline C₁₄H₁₅NaSNO₄, whence acids separate NHPh CS CH(CO₂Et), [60°] (Michael, Am 9, 124)—18 Urea dissolves in malonic ether and rhombic prisms of CHNa CO-NH CO sepa rate, whence acids liberate barbituric acid (Michael, J pr [2] 35,456) -19 Thro wrea gives similarly flat plates of sodium thio barbiturate CHNa CO-NH CS, whence acids liberate thiobarbituric acid, which crystallises in six sided plates from water -20 Acetamide forms crystalline C₁O₄N₂Na₂H₃, the reaction which occurs being 2CHNa(CO₂Et)₂+2CH₃CO NH₂ = C₀Na₂Na₂N₃H₄+CH₂(CO₂Et)₂+2HOEt -21 CSCl₂ forms CS C(CO₂Et)₂, which crystallises in flesh coloured needles [178°] (Bergreen, B 21, 337) – 22 Iodine forms (CO₂Et)₂CH CH(CO₂Et) Di bromo maleic ether yields 'di malonyl maleic' ether [75°], whence by saponification the corresponding acid C10H8O12 [148°] may be obtained. This acid, the formula of which is (CO₂H)₂CH C(CO₂H) C(CO₂H) CH(CO₂H)₂, may be better called butylene hexa-carboxylic acid It crystallises in plates, v sol water, and forms the salts, Na_eA^{vi} 10aq and Ag_eA^{vi}, and the ethers Me_eA^{vi} [129°] and Et_eA^{vi} [75°] (Pum, M 9, 450) When the acid is heated it splits up into CO2 and butylene tetracarboxylic acid CO₂H CH₂C(CO₂H) C(CO₂H) CH₂CO₂H [176°] 24 Dry cyanogen chloride forms cyano malonic ether (Halles, A Ch [6] 16, 419)

Di-sodium - malonic ether CNa₂(CO₂Et)₂. Obtained by ppg malonic ether (1 mol) with NaOEt (2 mols) (Bischoff a Rach.

B 17, 2782) Very unstable lodine converta

Ethyl propyl ether EtPrA" (211°)

SG § 10498 SV 2078 (Wiens, A 253, 297)

Propyl ether PrA" (228°) S G § 10271 S V 234 6 (Wiens, A 253, 297) S H (from 11 6° to 82 3°) 453 (R Schiff, G 17, 286)

Butyl ether (U4H,)2A" (251 5°) 049 SV 269 1 (Wiens, A 253, 297) 1 0049

Chloride CH₂(COOl)₂ (58° at 27 mm) From malonic acid and CSCl₂ heated above 100° (Béhal a Auger, Bl [2] 50, 594) Liquid Smells slightly like chloral

Amide CH₂(CONH₂)₂ [170°] (Van't Hoff, Ar Néerl 10, 274) S 83 at 8° (Henry, Bl [2] 43, 618) From malonic ether (50 c c) by shaking with strong aqueous NH, (150 c c) (Osterland, B 7, 1286, Freund, B 17, 133) The yield, in 2 days, is 75 pc Silky needles (from dilute alcohol), insol alcohol and ether Boiling aqueous NH, converts it into ammonium ma

lonamate white amorphous powder, insol alcohol and ether, sl

sol hot water, v sol HClAq (Freund) Di-methyl amideCH2(CO NHMe), [128°] (F), [125°] (Henry), [136°] (Franchimont, R T C 4, 199) Formed by the action of methylamine on malonic ether (Freund, B 17, 133) Small flat needles V e sol water and alcohol, sl sol ether Fuming HNOs converts

it into CH₂(CO N(NO₂)Me)₂ [150°]
Di-ethyl amide CH₂(CO NHEt)₂ [149°] Six sided tables (Wallach a Kamenski, B 14,

Ethylene dramide CH₂ CO NH C,H,

Formed by heating malonic ether or malonamide with ethylene diamine (Freund, B 17, 137) V sol water, nearly insol Crystalline solid alcohol

Amide-anilide CONH, CH, CONHPh [163°] Obtained by heating malonamide with 1 mol of aniline for ½ hour at 200°-220° (Freund, B 17, 135) Fine white felted needles hot water and alcohol

Mono an ilide CO2H CH2 CO NHPh Phenyl-malonamic acid Malonanilic acid Malonphenylamic acid [132°] Formed by boiling the amide anilide with milk of lime (Freund, B 17, 135) Formed also by heating sodium acetyl phenyl carbamateC,H,NAc CO,Na for 5 or 6 hours at 130°-140° under pressure (Seifert, B 18, 1359), and by heating malonic acid (1 mol) with aniline (1 mol) at 105° (Rug heimer, B 17, 737) Large colourless monoclinic crystals, or slender needles At its melting point it breaks up quantitatively into CO2 and acetanılıde - A'Ag small white needles -

acetanniae — A A A A'ga large needles A'ga large needles Ethyl ether of the mono-anrilede CO_Et CH_CONHPh [89°] From annine and Argelved in benzene CO2Et CH2 COCl, both dissolved in benzene (Rugheimer a Hoffmann, B 17, 739) Crystals (from ether-ligroin) Lisol water and ligroin, v e sol alcohol and benzene

Anilide CH2(CONHPh)2 [223°] tained by boiling malonic ether or malonamide with aniline (Freund, B 17, 184) needles Insol water and ether, e sol hot

Tri-bromo anilide CH₂(CO NH C₄H₂Br₆)₂ [146°] White silky needles, sl. sol alcohol, insol water (Freund, B White silky

Methyl-anilide CH2(CO NMePh)2 [109°] Obtained by boiling malonic ether with an excess of methyl aniline (Freund, B 17, 137) Colour-V sol alcohol

less trimetric prisms

Mono o-tolurde [2 1] CH, C,H, NH CO CH, CO,H o-Tolyl malonamic acid Colourless needles, v sol water and alcohol Melts about 140°, giving off CO2small needles, m sol water — needles, sol water — CuA'₂2aq BaA', aq prisms (Rugheimer a Hoffmann, B 18, 2971)

Ethylether of the o toluide EtA' [74°]

Long needles, sol ether and ligroin

Mono m tolurde [8 1]CH, C,H, NH CO CH, CO,H [1019.

Mono-p toluide

[4 1]CH, C,H, NH CO CH, CO,H Obtained by heating malonic acid with p toluidine (Rugheimer a Hoffmann, B 17, 740, 18, 2971) Long colourless needles, sol water, alcohol, ether, and chloroform At 150° it gives off CO₂ PCl, converts it into trichloro methyl quinoline 134°]—CaA', 24aq long needles, m sol water—BaA', 5aq needles—AgA' cheesy white pp or needles, sl sol water—CuA', 2aq minute needles, sl sol hot water—ZnA', glistening plates, m sol water

Ethyl ether of the p-Toluide EtA'

plates, v sol alcohol

Mono phenyl hydrazide
PhN₂H CO CH₂ CO₂H [154°] Formed from
malonic acid and aqueous phenyl hydrazine acetate at 100° (Fischer a Passmore, B 22, 2734) Needles, v sol water Its phenyl hydrazine salt PhN₂H₂ CO CH₂ CO₂N₂H₄Ph is converted at 200° into CH₂ CO N₂HPh, crystallising in white needles, [128°], v sol alcohol

Di phenyl dihydrazide

CH₂(CO N,H Ph)₂ [187°] From malonic ether or the amide of malonic acid and phenyl hydraz ine at 200° (Freund a Goldsmith, B 21, 1241) Plates (from dilute alcohol) With COCI, it gives C₁ H₁₂N₄O₄, which crystallises from HOAc in laminæ [205°]

Semi nitrile CO.H CH. CN v CYANO

ACETIC ACID

Netrile CH₂(CN), Methylene cyanule [80°] (219°) (H), (223°) (Berthelot a Petit, A Ch [6] 17, 131) HF -43200 Obtained by heating cyano acetamide CN CH₂CONH₂ with P₂O₅ (Henry, C R 102, 1394, 1481) White Appears to be polymerised by prolonged action of heat Sol water, v sol alcohol and ether Burns with a purple edged flame Conc HClAq dissolves it with evolution of heat and formation of malonic acid HClAq at 150° in sealed tubes forms CO2 and chloro acetic acid With ammoniacal AgNO, it gives a white pp CAg₂(ON), (?), which explodes when heated

References — Amido-, Bromo-, Chloro-, Cyano-, Nitro-, Methyl, Ethyl, Propyl-, Methyl ethyl, and Benzyl Malonic acid MALONYL-URRA v Barbituric acid

co<NH CH NH CH >C OH Isomalonylurea formed, together with amido uracil, by reducing

nitro-uracil (Behrend, A 229, 89, B 21, 999) It is converted by bromine into an acid isomeric with dialuric acid. The acetyl derivative C4H2N2O2Ac crystallises from hot water in prisms

MALONOXYL-AMIDO-BENZENE v CARB

OXY PHENYL MALONAMIC ACID

MALTOBIONIC ACID C12H22O12 Formed by oxidising maltose (1 pt) by bromine (1 pt) in water (7 pts) (E Fischer a Meyer, B 22, 1941) Almost colourless syrup V sol_water, sl sol alcohol, insol ether It reduces Fehling's solu tion By heating with dilute sulphuric acid it is split up into dextrose and gluconic acid

Salt -CaA', hard shining mass, v sol water

MALTONIC ACID Identical with GLUCONIC MALTOSE v SUGAR

MALYL TREIDE, so called, TURAMIDO SUCCINIC ACID

MANDELAMIDINE C.H.ON.O 2 e C_6H_5 CH(OH) C(NH₂) NH [110°] From the hydrochloride of mandelic imido ether and alco holic NH, (Beyer, J pr [2] 31, 387) Needles, v sol water and alcohol, al sol ether Very

unstable -B'HCl [214°] Prisms (from cold

water'

MANDELAMIDOXIM C.H. N.O. & 6 C.H. CH(OH) C(NH₂) NOH [159°] From the nitrile of mandelic acid and hydroxylamine (base) (Tiemann, B 17, 126) Crystals (from alcohol) Insol benzene, sl sol cold, v sol hot, water V e sol aqueous acids and alkalis colours its aqueous solution blood red. It does not reduce Fehling's solution

Reactions —1 The hydrochloride, mixed

with conc aqueous potassium cyanate forms C₂H, CH(OH) C(NOH) NH CO NH₂ [127°] — 2 Phenyl cyanate forms the corresponding Ph CH(OH) C(NOH) NH CO NHPh [155°] -3 Excess of AcCl, or a mixture of Ac2O and NaOAc forms C.H., CH(OAc)C NO CH.

[52°] -4 COCl, added to its benzene solution, forms (C.H. CH(OH) C(NH2) NO)2CO [131°] -5 Chloroformic ether, ClCO, Et, gives the com pound C.H. CH(OH) C(NH2) N O CO2Et [107°]

Salts -NaA' needles -HA'HCl (Gross, B 18, 1074)

Ethyl ether EtA' [89°] Slender needles, sl sol cold water With phenyl cyanate it forms Ph CH(OH) C(NOEt) NH CO NHPh [119°]

Bensyl ether C.H.CH.A' [103°] From mandelamidoxim, NaOEt, and bensyl chloride

(Gross, B 18, 1080) Needles

Acetyl derivative [140°] C.H. CH(OH) C(NH.) NOAc mandelamidoxim and Ac₂O Crystals (from alcohol) Insol cold water, sol alcohol, ether, and benzene With water at 100° it forms

 $C_{\bullet}H$, CH(OH) $C \leqslant_{NO}^{N} \geqslant C CH_{\bullet}$ [65°].

Di-acetyl derivative CaHaCH(OAc) C(NH2) NOAc C₆H₂CH(OAc) C(NH₂) NOAc [113°] From mandelamidoxim and a slight excess of AcCl Laminæ (from alcohol)

Bensoyl derivative C3H, CH(OH) C(NH2) NOBz From mandelamidoxim and BzCl (1 mol.) With AcCl it gives CaH, CH(OAc) C(NH2) NOBz [165°]

MÁNDELIC ACID C_sH_sO_s 2*6*

C.H., CH(OH) CO.H. Phenyl - glycollic acid Oxy-phenyl acetic acid Mol w 152 [115°] (Müller, Ar Ph [3] 2, 385), [118°] (Claisen, B 10, 847, Lewkovitch, B 16, 1568) S G ± 1 361 SG 41361 (Schröder, B 12, 1612) S 16 at 20° Heat of solution -3100 Heat of neutralisation by NaOH +13860 (Berthelot, A Ch [6] 7, 185) Formation —1 Discovered by Winckler (A

18, 310), who obtained it by heating bitter almond water with HCl, the benzoic aldehyde reacting with the HCy present (Liebig, A 18, 319) -2 By neating amygdalin with fuming HClAq (Wohler, △ 66,238) —3 By boiling the compound of benz oic aldehyde with KHSO, for several hours with KCy and alcohol The nitrile C₆H₅ CH(OH) CN thus formed is saponified by dilute HClAq (O Müller, B 4, 980) — 4 By reducing phenyl-glyoxylic acid C₂H, CO CO₂H with sodium-amalgam (Schwebel, B 10, 2045) — 5 From di-bromo acetophenone C₆H₅ CO CHBr₂ by boil ng with dilute KOHAq (120), the compound C_cH₁CO CH(OH)₂ being a theoretical intermediate product (Engler a Wohrle, B 20, 2202)—6 In small quantity, by boiling pseudo phenyl hydantom with baryta (Pinner, B 21, 2327) -7 By boiling a chloro phenyl-acetic acid with alkalis (Spiegel, B 14, 239)

Preparation — Benzoic aldehyde (100 g), water (3500 c c), fuming HClAq (200 g), and 4 times the calculated quantity of hydrogen cyanide are boiled for 36 hours The product is evaporated at 100°, the residue extracted with ether, the extract evaporated, and the mandelic acid left recrystallised from water (Wallach, A 193, 38, cf Strecker, A 75, 27)

Properties — Large trimetric crystals, v sol water, alcohol, and ether Inactive to light By crystallisation of the cinchonine salt it can be separated into equal quantities of the dextroand lavorotatory acids If Penicillium glaucum is grown in it the levorotatory acid is destroyed, leaving the dextrorotatory (Lewkowitsch, B 16,

Reactions -1 KMnO, and KOH convert it, in the cold, into phenyl glyoxylic acid (R Meyer a A Baur, A 220, 39) -2 Dry distillation yields benzoic aldehyde -3 Boiling with MnO₂ and H.SO, yields benzoic aldehyde and CO. -4 Fum ing HBrAq converts it slowly in the cold, quickly at 125°, into a bromo-phenyl-acetic acid, whence alcoholic NaOEt forms the ethyl derivative of mandelic acid (Glaser a Radziszewsky, Z [2] 4, 140) —5 Fuming HClAq at 140° gives a-chloro phenyl-acetic acid —6 Phosphorus and HI reduce it to phenyl acetic acid -7 When taken mternally it passes unaltered into the urine (Schotten, H 8, 68) —8 Cannot be nitrated Conc NHO, forms benzoic aldehyde (Liebig, A. 18, 321), dilute HNO, forms phenyl glyoxylic acid (Zincke a Hannaus, B 10, 1488) —9 Dilute H.SO, in sealed tubes at 130° converts mandelic acid nearly quantitatively into benzoic aldehyde and formic soid (Biedermann, B 19,638) 10 Chloral at 120° forms

$$C^H$$
 CH $<_0^{COO}>$ CH CCI

which forms large transparent crystals [83]. msol water, sol. alcohol and chloroform (Wal-

lach, A 193, 1) -11 Phenyl-hydrasme forms a compound [182°], crystallising in needles and almost msol boiling water (Reissert a Kayser, B 22, 2928)

Salts —The ammonium and potassium salts are very soluble and difficult to crystallise The Ba salt forms small needles S 8 at 24° 16 at 100° (Zinin, Z 1868, 710) The lead salt is a crystalline powcer, scarcely sol water — CuA'₂ (dried at 100°) — AgA' crystalline pp

May be crystallised from water

Methylether MeA' [48°] Small laminæ (from benzene-ligroin) (Zincke a Breuer, B 13,

Ethyl ether Ph CH(OH)CO.Et Formed by the action of water on the hydrochloride of man lelic imido ether (q v)Solidi fies in a freezing mixture, but is liquid at ordinary temperatures (Beyer, J. pr. [2] 31, 389) But Naquet and Luguinin (A. 139, 300), who prepared it from silver mandelate and EtI, say it melts at 75°

Methyl derivative Ph CH(OMe)CO H [72°] Formed from Ph CHCl CO Me, MeOH, and NaOMe (R Meyer a H Boner, A 220, 44, B 14, 2392) Needles grouped concentrically (on solidifying) or thick tables (from light petro-V sol alcohol or ether, sl sol cold KOH and KMnO. water or cold petroleum forms phenyl glyoxylic acid Salts — NaA'2aq — BaA'22aq — CaA', —

CuA'22aq -AgA'

Methylether of the methyl derivative

Ph CH(OMe) CO Me (246° cor)

Ethyl derivative C₆H, CH(OEt) CO₂H

From C₆H, CHBr CO₂H and alcoholic KOEt

Viscid mass -AgA' pulverulent pp Phenyl derivative Ph CH(OPh) CO₂H [108°] From methyl a chloro phenyl acetate and sodium phenate (R. Meyer a. H. Boner, A. 220, 51) Radiating groups of slender needles (from water) V sl sol cold water, v e sol alcohol or ether KOH and KMnO, convert it into phenyl glyoxylic acid HNO, forms pieric acid and benzoicaldehyde -NaA', 3aq -CuA', -

Acetyl derivative of the ethyl ether C.H. CH(OAc) CO2Et [74°] From mandelic acid by successive treatment with AcCl and alcohol (Naquet a Luguinin, A 139, 302) Slender needles (from ether) Insol. water, v sol alcohol and ether

Amide C.H. CH(OH) CONH, [132°] S 3 at 24° S (boiling 93 pc alcohol) 100 (Z) Formed, together with benzoic aldehyde, by heating the compound (C.H. CHO) CNH with water or alcohol at 180° (Zinin, Z [2] 4, 709) Formed also by allowing a mixture of the nitrile with fuming HClAq to stand in the cold (Tie mann a Friedlander, B 14, 1967) Likewise obtained by the action of NH, on mandelic ether, and by heating mandelic imido-ether (C Beyer, J pr [2] 31, 386) Prismatic needles or plates Sol hot, al sol cold, water, al sol ether, v sol alcohol Decompose by acids and alkalis with production of mandelic acid A polymeride (?) melts at 190°

Nutrule CeHsCH(OH) CN [-10°] 1 124 Obtained by adding furning HClAq to a mixture of benzoic aldehyde and KCy (Spiegel, B 14, 239, Völkel, A 52, 861) Oil, sol alcohol and ether Dissolved in ether, mixed with alcohol (1 equivalent), and treated with HCl gas at forms C₄H₃ CH(OH) C(OEt) NH,HCl [125°] This is decomposed by water, forming NH,Cl and mandelic ether (Beyer, J pr [2] 28, 190) At 170° mandelonitrile splits up into benzoic aldehyde and HCy Boiling aqueous HCl gives NH,Cl and mandelic acid Fuming HClAq forms the amide in the cold, but on heating it gives a chloro phenyl acetic acid NH₃ in the cold forms C₄H₃ CH(NH₂) CN Methylamine yields C₄H₃ CH(NHMe) CN Phenyl hydrazine produces the phenyl hydrazide of benzoic aldehyde (Reissert, B 17, 1451)

(dextro) Mandelic acid [133° cor] [a]_b at 20° = +156 Prepared by converting inactive mandelic acid into the cinchonic salt and adding a crystal of cinchonine dextro mandelate to the aqueous solution when the dextro salt crystallises out, leaving the lævo salt in solution. It can be also obtained by growing Penicillium glaucum in the inactive acid, which destroys the lævorotatory acid, leaving the dextrorotatory (Lewkowitsch, B 16, 1568) Resembles the lævoacid, having the same solubility in water

(larro)-Mandelic acid [133°] S 864 at 20° [a]_D at 20° = -158 Prepared by heating amyg dalin with strong HCl for several hours on the water bath It can also be obtained from in active mandelic acid which can be separated into equal quantities of the lævo and dextrorotatory acids by crystallisation of the cinchonine salt (Lewkowitsch, B 16, 1565, cf Wöhler, A 66, 240)

Nitro mandelic acid v Nitro OXY-PHENYL-

MANDELIC IMIDO ETHER

Ph CH(OH)C(NH)OEt [72°]

Preparation — Benzoic aldehyde (100 g) treated with KCN, dilute HCl and ether forms the exanhydrin Ph CH(OH)CN which is dissolved by the ether. If this is mixed with an equivalent of alcohol and dry HCl be passed in, the liquid being cooled, needles of the hydrochloride of mandelic imido ether (80g) are formed (C Bever, J pr [2] 31, 3*4) Ph CH(OH) CN+EtOH+HCl = PhCH(OH) C(NH) OEL, HCl These melt at [125°] The free ether is got by shaking these simultaneously with cone KOH and ether After evapor tring the ether the residue is crystal lised from ligroin

Projecties — White needles Extremely soluble in ether, alcohol, and benzene

Reactions —1 At 140° the hydrochloride splits up thus PhCH(OH)C(NH)OEt,HCl = EtCl+PhCH(OH)CONH,, forming mandel-amide —2 Alcoholic NH, converts the hydrochloride into the hydrochloride of the amidine, PhCH(OH)C(NH)NH,HCl This forms prisms [214°] Shaken with ether and potash, the free mandel amidine, *PhCH(OH)C(NH)NH, is dissolved by the ether It forms feathery needles of narcotic odour, melting at [110°]—8 Water quickly converts the hydrochloride into mandelic ether (q v) C,H,CH(OH) C,NH)OEt,HCl+H,O = C,H,CH(OH) COOEt+NH,HCl

MANDRAGORINE C, H₂₁NO, [e 79°] Extracted from powdered mandragora root by alcohol The extract is evaporated and the residue treated with very dilute acid The alkaloid is liberated from the acid solution by Vol. III

adding K₂CO₃ and shaking with ether (Ahrens, A 251, 312) Hygroscopic brittle mass Pierra card gives with a solution of mandragorine hydrochloride light yellow needles of the pierate. Iodine in KIAq gives an oily periodide K₄FeCy, gives no pp Phosphotungstate gives a white pp The sulphate is crystalline and very de liquescent Dropped into the eye, its solution causes enlargement of the pupil —B'HAuCl₄· [155°], yellow plates, sol hot water and HClAq —B'₂H₂PtCl₄, [194°] Red nodules or yellow plates (from hot water) —B'HCl4HgCl₂· [160°] Plates or needles (from water) or long slender needles (from alcohol) V sol alcohol (Ahrens, B 22, 2161)

Mandragora root also contains a second alkaloid of which the platinochloride [181°] and aurochloride [147°-153°] are crystalline (Ahrens)

MANGANATES Salts of the form MI₂MnO₄ derived from the hypothetical acid H₂MnO₄, v. Manganese, oxyacids or, p 185
MANGANESE Mn At w 55 Mol w

MANGANESE Mn At w 55 Mol w probably same as At w (v infra) [c 1800°–1900°] S G 6 85 to 8 01, according to Glatzel, S G of pure Mn is 7 3921 at 22° (B 22, 2857) S H 14° to 97° 1217 (Regnault, A Ch [3] 67, 427, specimen contained Si) Chief lines in emission spectrum are 6521, 6016, 6013, 4823, 4763, 4765, 4762, 4753, 4235, 4027 (Thalén) For absorption spectrum of Mn vapour v Lock yer a Roberts (Pr 23, 344)

Occurrence—The metal does not occur uncombined Mn compounds are widely distributed, the chief are pyrolusite MnO₂, braunite Mn.O₃, manganite Mn.O₄, H.O., hausmannite Mn₃O₄, psilomelane (Mn,Ba,K.)O 4MnO₃, manganese Spar MnCO₃, manganese blende MnS small quantities of Mn compounds are found in sea water (Forchhammer, Pr E 2, 303), in many mineral waters (Buchanan, Pr 24, 593), in blood (Cottereau, J 1849 530, Burin de Buisson, J 1852 377, Campani, B 5, 287), in the liver (B(champ, C R 49, 895), in milk (Polacci, Naturforscher, 4, 122), in human urine (Horsford, J 1851 602), in wines, cereals, most veretibles used as human food, and in considerable quantities in tea (Maumené, C R 98, 1050, 1410) Mn also occurs in the sun's atmosphere (Coinu, C R 80, 315, 530)

Manganese dioxide was recognised as a compound of a distinctive metal by Scheele in 1774, it had pieviously been looked on as a compound of iron. The metal Mn was first isolated by Gahn Native MnO was long known as magnesia nigra (probably because of its supposed magnetic properties), a new medicine was introduced in the early years of the eighteenth century, and was called magnesia alba, seemingly in contra distinction to magnesia nigra, when magnesia nigra was shown to contain a distinctive metal, this metal was called sometimes magnesium and sometimes magnesium and sometimes magnesium was retained for the metal of magnesia alba, and the name manganesium (hence manganesis) was given to the metal of magnesia nigra.

Formation —1 By reducing the oxides by C at a white heat.—2 By reducing MnF₂ or MnCl₂ by Na or by Mg —3 By heating Mn amalgam is a stream of H, the amalgam is made by the reaction of Na amalgam with MnCl₂Aq (Giles,

P M [4] 24, 328, Roussin, Bl 6, 93) —4 By electrolysing MnCl.Aq in a porous cell placed in a carbon crucible containing HClAq (Bunsen, P.

Preparation — 1 Crystallised MnCl₂ is thoroughly dried by heating, it is then finely powdered and 100 grams are intimately mixed with 200 grams well dried and powdered KCl, the mixture is packed into a Hessian crucible which is loosely covered and heated in an airfurnace until the contents melt (the temperature must not be raised so high that white vapours begin to come off), the lid is removed and 15 grams Mg are thrown into the crucible in four or five portions, each weighing 3 to 4 grams, two to three minutes being allowed to elapse between the entrance of each piece, the lid is now replaced and the crucible is strongly heated for a few minutes, and then allowed to cool very slowly in the furnace About 20 to 25 grams Mn are thus obtained as a compact regulus If the temperature of the final heating is not sufficiently high, the regulus does not form a compact mass, if the temperature is too high and the heating is unduly prolonged, the KCl is vaporised and the surface of the Mn is oxidised (Glatzel, B 22, 2857) —2 Brunner (P 101, 264) recommends the following method -2 pts MnF₂ (obtained by dissolving moist MnCO₃ in HFAq, evaporating and drying at 100°) and 1 pt Na are arranged in alternate thin layers in a Hessian crucible, the mixture is pressed down and covered with NaCl over which is placed a layer of CaF2 in small pieces (to prevent spirting), the crucible is covered and heated in an air furnace, at first gently, and then to near a white heat for about 1/4 an hour, the crucible is then allowed to cool very slowly in the furnace - 3 For an account of the older methods of preparing Mn from MnO2, v John (Gehlen's Journ Chem Phys 3, 452), and Deville (A Ch [3] 46, 182) Tamm describes a method for obtaining approximately pure metal (99 91 pc Mn, 05 pc Fe, 115 pc Si, and 025 pc C) from MnO₂ (C N 26, 73, 111)

Properties —A white grey, lustrous, metal, very hard, brittle, may be highly polished, non magnetic (Glatzel) According to Glatzel (B 22, 2857), Mn prepared by reducing MnCl, by Mg (v Preparation No 1) is unchanged by keeping for months in a bottle closed with a glass stopper, but in moist air the surface undergoes slight oxidation Mn is usually described as very easily oxidised in ordinary air, and as capable of decomposing water, with evolution of H, almost as rapidly as K Mn obtained by Brunner (vPreparation No 2) by reducing MnF₂ by Na was scarcely oxidised in cold water According to Bullock (C N 60, 20), Mn prepared by reducing the oxides by C is very easily oxidised, while specimens obtained by reducing MnCl₂ by Na are no more oxidisable than iron. It is probable that some specimens have contained small traces of S1 and C which have affected the properties of the metal Mn melts at a very high temperature (c 1800°-1900°), and is said to volatilise at a full white heat

The atomic weight of Mn has been determined (1) by estimating Cl in MnCl₂ (Arfvedson, S 42, 202, Dumas, A Ch [3] 55, 151; Berzelius, P. 18, 74), (2) by dissolving Mn in HNO₂,

evaporating, and calcining the nitrate (Berzelius, P 8, 185), (3) by oxidising MnO to Mn,O, by heating in air (v Hauer, W A B 25, 133), (4) heating in air (v. Hauer, W. A. B. 20, 150), (4p) by reducing Mn₂O₄ in H, and weighing H₂O produced (Rawack, P. 107, 605, 616), (5) by analysing MnC₂O₄ (Schneider, P. 107, 605), (6) by reducing AgMinO₄ and estimating Ag produced (Dewar a Scott, Pr. 35, 44), (7) by determining S H (Regnault, A. Ch. [3] 67, 427)

Molecular weight of manganese—Ramsay (2, 7, 55, 591) her determined the lowering of

(O J 55, 521) has determined the lowering of the vapour pressure of Hg produced by dissolving Mn in Hg, the results render it probable that the molecular weight of Mn is the same as the atomic weight. This conclusion assumes the accuracy of Van't Hoff's law that equal volumes of dilute solutions contain equal numbers of molecules of the dissolved substances, and it also supposes the molecular weight of liquid Hg to be the same as the atomic weight of Hg

Mn is metallic in its physical, and some of its chemical, properties, but in many of its ieactions it behaves as a non metal The oxides MnO and Mn₂O₃ are basic, forming salts, such as MnSO₄ and Mn₂(SO₄)₃, of which the man ganous salts, corresponding with MnO, are much the more stable The oxide MnO reacts as a basic peroxide, e g with H2SO, it forms MnSO. and O, it lso reacts with some positive oxides, $e\,g$ CaO, to produce salts of the form xMO yMnO , when this oxide is treated with molten KOH in presence of O the salt K.MnO. is formed, in which Mn forms part of the acidic radicle The oxides MnO₃ and Mn O₇ have also been isolated, both are very unstable, both react with water to form manganic acid HMnO. the former (MnO₃) at the same time also producing MnO., these oxides are distinctly acidic The acid HMnO, has been isolated, and many salts derived from the hypothetical acid H MnO. are known

Mn shows marked analogies with the iron metals Fe, N1, and Co, 1t 1s also related, although less distinctly, to the halogens, and it is also related to the chromium metals, Cr, Mo, W, In the classification of the elements based on the periodic law, Mn occupies a position different from that of any known element it is placed in the same group as the halogens (Group VII), and in the same family (evenseries members) as F, but no member of this family coming after Mn (i.e. with a greater atomic weight than Mn) has yet been isolated, Mn finds a place in series 4 (K, Ca, Sc, Ti, V, Cr, Mn), all the members of which are metallic, and it is immediately followed by Fe, Ni, Co, and Cu The strongly marked negative charac ter of the halogens is impressed on Mn, but this is counterbalanced by the positive characteristics of the metals which come before and after Mn in order of atomic weights (v Halogen ele MENTS, vol 11 p 666, also Iron GROUP OF ELE-MENTS, this vol p 65)

The atom of Mn is divalent in the gaseous

molecule MnCl₂.

Reactions —1 Mn is oxidised in air or oxy gen, forming MnO -2 Mn reacts energetically with dilute mineral acids forming salts of MnO 3 Fused with potassium nitrate or chlorate KMnO41s produced -4 Heated in bromine MnBr. is formed -5 When Mn is heated in a stream of hydrogen chloride MnCl₂ is produced —6 Mn decomposes water readily, with evolution of H. The reactions of the metal have not been much examined

Combinations -Mn forms alloys with many metals, and compounds with most of the non metals, but few have been formed by the direct union of their elements

Detection and estimation -Mn is usually detected by the colour its' compounds impart to a borax-bead, and by the ppn of buff-coloured MnS by addition of NH, sulphide to an alkaline Mn is usually or neutral solution of Mn salts estimated gravimetrically by ppn with NH3Aq, heating the pp in air, and weighing as Mn.O. As MnO2 is much used in technical chemistry it is necessary to have accurate and rapid methods for determining the quantity of this oxide in specimens of Mn ores, for descriptions of these methods, and also for other methods for estima ting Mn, reference must be made to Manuals of

Manganese, alloys of Several alloys of Mn have been prepared, none has been made by

directly alloying Mn with other metals

1 With aluminium Wöhler a Michel (A 115, 102) obtained a crystalline powder, having the composition MnAl,, by fusing together MnCl2, Al, and a mixture of NaCl and KCl

- 2 With copper Alloys of Mn and Cu are obtained by reducing mixtures of MnO, and Cu with charcoal, an alloy containing 25 pc Mn is white, fairly haid, very elastic, and tolerably easily melted (Allen, C N 22, 184) Alloys con taining from 3 to 20 pc Mn resemble bronze (Valenciennes, C R 70, 607, v also Schrötter, D P J 210, 355, Prieger, ibid 177, 303, Gintl, sbid 221, 653)
- 3 With iron Alloys of Mn and Fe, containing from 8 to 80 p c Mn, are used in the manufacture of steel, under the names of spiegeleisen These alloys are prepared and ferromanganese by heating MnO with non filings and charcoal in the blast furnace, or in graphite crucibles, or by reducing a mixture of FeO and MnCO, on the hearth of a Siemens' furnace, and then fusing under a reducing flame
- 4 With mercury An amalgam of Mn is obtained by reducing MnCl2Aq by Na amalgam (Giles, P M [4] 24, 328), also by electrolysing MnCl₂Aq in contact with Hg (Ramsay, C J 55, 532, Moissan, Bl [2] 31, 149) Alloys of Mn with Pb, Sn, and Zn are described by Allen (lc) and Valenciennes (lc)

Manganese, arsenates of, v vol 1 p 309 Manganese, arsenade of Mn and As com bine when heated together to redness An arsenide, approximately As₃Mn₄, occurs native (Kane, P 19, 145)

Manganese, arsenite of, v vol 1. p 306 Manganese, boride of By heating Mn.C

(v Manganese, carbides of) with B,O, in a graphite crucible, Troost and Hautefeuille obtained small greyish violet crystals of MnB₂ (C R 81, 1263) This compound decomposes water at 100° and dissolves in acids with evolution of H, it reacts with moist HgCl, to produce MnCl, boric acid, and HCl

Manganese, bromides of Only one bromide. MnBr., has been isolated, the tetrabromide also perhaps exists in solution

MANGANOUS BROMIDE, MnBr. Manganese romide The hydrate MnBr. 4H₂O is obdibromide tained as clear, red, deliquescent, crystals, by dissolving MnCO, in HBrAq, or by digesting Mn with Br (Balard, J pr 4, 178, Marignac, Ann M [5] 12, 7), crystallises in monoclinic forms, a b c = 645 1 1 165 (Marignac) The anhydrous salt MnBr, is obtained by heating powdered Mn in Br vapour, it forms a rose red deliquescent mass, heated in air it gives Br and Mn,O4 Thomsen gives the thermal data -[Mn, Br2, Aq] =106,120 (Th 3, 271)

MANGANIO BROMIDE, MnBr. (Manganese te-bromide) This compound perhaps exists in trabromide) the green solution obtained by treating Mn.O. or MnO, with HBr gas and dry ether, the solution is easily decomposed with formation of MnBr. (Nicklès, C R 60, 79)

Manganese, carbides of According to Brown (J pr 17, 492), the compound MnC is obtained by heating Mn(SCy)2, and MnC, by heating MnCy2. Troost and Hautefeuille obtained graphite-like, lustrous, crystals of Mn₃C by melting Mn in a charcoal crucible, and cooling slowly (C R 80,

Manganese, chlorides of The only chloride of Mn which has been isolated is MnCl. A solution of MnO2 or Mn2O3 in conc cold HClAq very probably contains Mn2Cl8, perhaps also some The existence of MnCl, described by MnCl,

Dumas, is very doubtful

Manganous chloride, MnCl₂ Mol w 125 74, Rose-coloured crystals of MnCl 4H O are ob tained by dissolving MnCO, or any oxide of Mn, in HClAq, and evaporating, by heating the dried crystals in a stream of dry HCl, the an hydrous salt, MnCl₂, is obtained MnCl₂ is also formed by heating Mn, MnCO₃, or Mn₃O₄, in a stream of dry HCl By heating very finely powdered MnO with half its weight of NH,Cl gradually to redness, MnCl, is formed very deliquescent, Brandes (P 22, 263) gives S at $10^{\circ} = 62 \, 16$, at $31 \, 25^{\circ} = 85 \, 72$, at $62 \, 5^{\circ} =$ 122 22, at 87 $5^{\circ} = 122$ 22, and at 106 $25^{\circ} = 123$ 81 S in alcohol at $11^{\circ} = 50$ S G of MnCl, = 2 478 (Schröder), of MnCl₂ 4H₂O = 1913 (Schröder), 2015 (Boedeker) The tetrahydrated salt is isomorphous with FeCl 4HO, monoclinic, All water is removed at 100° Thomsen the thermal a b c=1 1409 1 1 6406 (Marignac, 15) gives the thermal data $[Mn,Cl^2] = 111,990$ $[MnCl^2,Aq] = 16,010$, $[MnCl^2,4H,0] = 14,470$ (Th 3, 270) Heated in O, a crystalline oxide containing 37 p c MnO2 is produced (Schulze, J pr [2] 21, 407) MnCl, melts, in absence of air, at a red heat and sublimes at higher temperature Scott found V D at c 1200°-1500° to be 1323 $(Pr \ E \ 14, 410)$

MnCl, forms double salts with the alkall chlorides, of the composition MnCl. 2XCl 3H,O The best examined are those in which X = NH, Rb, and Cs, the NH, salt contains one H,O only according to Rammelsberg $(J \ pr \ 65, 181, \ con firmed by Pickering, <math>C \ J \ 85, 672)$ The double salts are obtained by mixing MnCl₂Aq or a solu The double tion of an oxide of Mn in HClAq, with the alkali chloride, and evaporating slowly (v Godefiroy, B 8, 9, v Hauer, J pr 63, 436) Another double salt MnCl, 3CuO 3H,O, is formed by boiling MnCl,Aq with powdered CuO, filtering, and cooling (André, C R 106, 854) The double salt MnCl₂ HgCl₂ 4H₂O, is described by Bons dorff (P 17, 131)

Manganic chloride, Mn_2Ol_4 , and Manganese Tetraceloride, $MnCl_4$ Neither of these chlorides has been isolated Mn_2O_4 and MnO_2 dissolved in cold cone HClAq to form deep-brown liquids, which slowly evolve Cl and after a time contain MnCl. Nickles (A Ch [4] 5, 161), by passing HCl into ether in which MnO₂ was suspended, obtained a green liquid, of varying composition and very unstable, one analysis gave results approximately agreeing with the formula MnCl, 12C,H₁₀O 2H₂O These results are quite inconclusive of the formation of MnCl, (cf Pickering, C J 35, 672) Fisher's experiments (C J 33, 409) led him to conclude that a solution of MnO2 in cold cone HClAq contains MnCl₄, but the more complete experiments of Pickering (C J 35, 654) make it very probable that Mn₂Cl₈, and not MnCl₄, is produced when either Mn₂O₃ or MnO₂ is dissolved in cold conc When the solutions are decomposed by adding water, the pp varies in composition but may always be expressed as $xMnO_2yMnO$, x varying from 16 to 36 and y being usually 5 Pickering expresses the reactions of HClAq with Mn₂O₃ and MnO₂, and the decomposition of the solutions by H.O, in the following equations -

 $\begin{array}{l} Mn_2O_3 + 6HClAq = Mn_2Cl_6Aq + 3H_2O \\ 2MnO_2 + 8HClAq = Mn_2Cl_6Aq + Cl_2 + 4H_2O \\ \{xMn_2Cl_6Aq + 2H_1O = MnO_3 + MnCl_6Aq + 4HClAq \\ \{yMn_2Cl_6Aq + 3H_1O = Mn_2O_3 + 6HClAq \\ \end{array} \right\}$

The average values of x and y are 4 and 1 respectively Christensen (J pr [2] 35, 57) thinks that $\mathrm{Mn_2Cl_8}$ is the product of the reaction of cold HClAq with MnO₂, he supposes that some MnCl₄ is produced at 10° According to C, ether holding HCl in solution produces a solution of Mn₂Cl₄ when shaken with Mn₂O₃ According to Vernon (C S Proc 1890 58), a solution of MnO₂ in cone HClAq evolves less than half the Cl, at ordinary temperatures, required by the equations given by Pickering (supra), at -18° Cl is evolved very slowly, and at -26° only 35 pc of the available Cl comes off when air is drawn through the solution for two hours Vernon thinks that MnCl₄ is the only higher chloride formed by dissolving MnO₂, Mn₂O₃, or Mn₃O₄ in cold cone HClAq

Franke (J pr [2] 36, 38) obtained chloromanganic acid, H.MnCl, by adding KMnO, to ether containing HCl, shaking with dry ether, and surrounding the deep-blue liquid thus pro

duced with a freezing mixture

Manganese Heptachloride, MnCl, (?) Dumas (B J 7, 112, 8, 177) described a greenish gas, condensing at — 15° to — 20° to a green brown liquid, produced by adding excess of cone H₂SO₄ to KMnO₄ and throwing in small pieces of fused KCl or NaCl, he gave the formula MnCl, to this substance Aschoff's analyses of the compound proved the presence of O in it, and led to the formula MnO₄Cl (J pr 81, 29) The exact composition of the substance is not yet settled.

Manganese, chromate of, v vol 11 p 155 Manganese, cyanides of, v vol 11 p 842 Manganese, ferri- and ferro cyanides of, v vol 11 pp 835, 839

Manganese, fluorides of Two fluorides of Min have been certainly isolated, Min, and

Mn₂F₄ The existence in solution of MnF₄ is doubtful Wohler obtained a gas by the reaction of H₂SO₄ with a mixture of K₂MnO₄ and KF To this gas he assigned the composition MnF₇, but the composition of the substance cannot be regarded as settled Nicklès asserts the existence of Mn₂F₈

MANGANOUS FLUORIDE, MnF₂ (Manganese ds-fluoride) A reddish crystalline powder, obtained by dissolving MaCO₂ in excess of HFAq and evaporating, undecomposed by heating to

redness (Berzelius)

MnF₂ forms double compounds with SiF₄, &c (Berzelius, Stolba, C \tilde{C} 1883 292, Marignac, J pr 83, 202) These compounds, better regarded as silicofluoride, titanofluoride, &c, of Mn, have the composition MnXF₆6H₂O, where $X = S_1$, T_1 , or S_1 , they are isomorphous, crystallising in hexagonal forms, ac = 1 515 (Marignac, Ann M [5] 15) There is also a zircofluoride of Mn, $MnZnF_6$ 5H₂O, which crystallises in monoclinic forms, ab c = 2 09 1 1 2515 (M l c)

MANGANTSE SESQUIFLUORIDE, Mn.F. Crystals of Mn.F. 6H,O were obtained by Christensen (Jpr [2] 35, 57) by dissolving artificially prepared MnO2 in HFAq, filtering through spongy Pt, evaporating, and placing over H₂SO₄. Boiling or diluting the solution of MnO2 in HFAq pro

duces an o yfluoride

The double salts Mn₂F₆ 4KF 2H₂O, Mn₂F₆ 4NH₂F, Mn F, 4NaF, and Mn₂F₆ 2AgF 8H₂O are described by Christensen (*lc* and *ibid* p 161) They are obtained by adding solution of the alkali fluoride to solution of Mn₂O₂ or MnO₂ in HFAq, washing with water containing HF, and drying on Pt, the Ag salt is obtained by dissolving freshly ppd Ag CO₂ in HFAq, adding Mn₂F₆ in HFAq, and evaporating Ac cording to Christensen, the salt Mn F, 4KF 2H.O is identical with the compound to which Nickles gave the formula MnF₄ 2KF (*C* R 65, 107)

Manganese tetra and hepta fluorides, MnF, and MnF, (?) The former compound was supposed by Nickles to exist in the solution of MnO, in HFAq (C R 65, 107), by adding kF or NaF the double salts MnF, 2K(Na)F were said to be formed The investigations of Christensen (J pr [2] 35, 57, 161) have made it very probable that MnF, and not MnF, is formed when MnO, or MnO, is dissolved in Hi Aq (v supra, cf Mangane chloride, supra)

The formula MnF was given by Wohler (P 9, 619) to a purple yellow gas obtained by adding cone H₂SO₄ to a mixture of 2 parts commercial K₂MnO₄ and 1 part CaF₂ in a Pt retort The gas dissolves in water to form HMnO₄Aq and HFAq, and on evaporation HF and O are evolved, and MnF₂ remains The composition of the gas is still very doubtful, no analyses are given in Wohler's paper

MANGANO MANGANIC FLUORIDE, Mn₂F₆ According to Nicklès (C R 67, 448), brown crystals, having the composition Mn₂F₆ 10H₂O, are obtained by reacting on MnO₂ with warm HFAq and evaporating

Manganese, haloid compounds of The compounds MnX₂(X = F, Cl, Br, I) have been isolated. Mn₂F₆ has also been obtained in definite form. There are very strong reasons in favour of the existence of Mn₂Cl₆ in the solutions obtained by dissolving Mn₂O₆ or MnO₂ in cold cone HClAq.

The existence even in solution, of tetra haloid | and then decomposed, the formation of higher compounds, MnX, is doubtful Nickles claims to have obtained mangano manganic fluoride Mn_3F_s , corresponding with Mn_3O_s . The only haloid compound of Mn which has been gasified is $MnCl_2$. The general formula MnX_2 probably expresses the atomic composition of the mole cules of the more stable haloid compounds of Mn, the formula Mn X_c may or may not be mole cular The existence of hepta-haloid compounds MnX, might be expected from the position of Mn in the periodic scheme of classification, but the existence of these compounds is extremely **dou**btful

Manganese, hydroxides of, v Manganese, oxides and hydrated oxides of, for HMnO, v

Manganese, oxyacids of

Manganese, 10dide of MnI_2 Obtained. with 4HO, in rose red deliquescent crystals, isomorphous with MnCl₂4H₂O, by dissolving MnCO₃ in HIAq, and evaporating Turns brown when exposed to air and light, heated in absence of air, it is not decomposed, heated in O it burns like tinder, evolving vapours of I Thom sen gives the thermal data [Mn, I^2 , Aq] = 75,700 (Th 3, 271)

Manganese, oxides and hydrated oxides of The oxides MnO, Mn₂O₄, Mn₂O₃, MnO₂, probably also MnO, and Mn,O,, have been isolated number of oxides intermediate between Mn,O, and MnO2, having the general form xMnO2 yMnO, also exist Hydrates of most of these oxides exist, but their stability is generally small Mn₂O, H₂O $= H_2Mn_2O_0$ is known, it is an acid The acid corresponding to MnO₃ (H,MnO₄) has not been isolated, but salts of this acid (manganates) are The oxides MnO, Mn₂O₄, and Mn₂O₃ MnO reacts with acids to form man ganous salts MnX_2 ($\lambda=NO_3$, $\frac{1}{2}SO_4$, &c), Mn_1O_4 forms manganic salts Mn_2V_3 , which are readily reduced to MnX_2 , Mn_3O_4 does not form corre sponding salts, but with acids yields Mn 1, and Mn X₃, or in some cases MnX₂ and MnO₂ Nickles, however, asserts the production of Mn₃F₆ by the action of HFAq on Mn₃O₄ (v Mangano manganic fluoride, p 180) MnO₂ reacts with acid to form manganic salts Mn₂X₃ MnO₂ or manganous salts MnX, according to tempera It is possible that a few salts correspond ing with MnO2 may exist, but their isolation is MnO, also combines with some oxides more basic than itself to form manganites, salts of the form $xMO yMnO_s$ MnO_s is very unstable, The existence of it does not form salts (MnO₃)₂SO₄ is probable With water MnO, forms H2Mn2O8Aq and MnO2 Mn2O, is very unstable, with water it forms permanganic acid, H2Mn2O.

The molecular weight of none of the oxides of Mn is known with certainty, as none has

been gasified

MANGANOUS OXIDE, MnO (Manganese monoxide or protoxide) S G 5 09, crystalline (Rammelsberg), 5 18, manganosite (Blomstrand, B 8,

Occurrence - In small quantities, as manganosite, in bright green hexagonal forms (Blomstrand, lc)

Preparation -1 By heating to redness in a Pt vessel a mixture of equal parts MnCl₂ and Na₂CO₃, with a little NH₄Cl, MnCO₃ is formed

oxides is prevented by the NH,Cl, the residue is washed and dried (Liebig a Wohler, P 21, 578) 2 By heating any of the higher oxides of Mn, very finely divided, to redness in a stream of H until the powder is green According to Wright a Menke (C J 37, 28), pure MnO can be thus obtained, even from specimens of MnO2 contain ing c 10 p c of potash - 3 MnCO₃ or MnC₂O₄ is strongly heated in absence of air, and the pro duct is then heated in H (Liebig, A 95, 116) 4 Deville (C R 53, 199) obtained MnO in bright green regular octahedra by heating MnO, in H

containing a very little HCl
Properties and Reactions — A grass green powder, Deville's crystalline specimen (v supra) formed lustrous, diamond like, green regular octahedra According to Moissan (A Ch [5] 21, 199, 251), MnO prepared by reduction of higher oxides by CO at 140° is pyrophoric When pure, MnO does not oxidise by exposure to air (Wright a Menke, C J 37, 28 note), but if it contains minute quantities of potash oxidation occurs Heated in air or O, Mn₂O₄ is produced, if the heating is done carefully till the weight is con stant at dull redness, Mn₂O₃ is produced (v Gorgeu, C R 106, 743) MnO melts at white heat in absence of air It is not reduced by heating in H or CO, or with C at 500° 600° (Wright a When heated in H.S. MnS Luff, C J 33, 523) and H₂O are formed MnO reacts with acids to form manganous salts, MnX₂ (X = NO₃, ClO₃,

1SO, 1PO, &c)

HYDRATE OF MANGANOUS OXIDE, MnO H2O Occurs in small quantities in Sweden, in white crystalline tablets, as pyrochroite Prepared, as small white hexagonal prisms, by adding 300 grm KOH in 500 c c air free water to an air free solution of 15-17 grm crystallised MnCl in 15 cc air free water, in a vessel filled with H or coal gas, heating to 160°, and allowing to cool (A de Schulten, C R 105, 1265) Rapidly oxi dises in air When a manganous salt is present the compound 2MnO MnO, xH2O is formed, when exposed to O for several years the product is MnO₂ MnO (Gorgeu, C R 108, 948) When NH, Aq is added to solution of a manganous sait, MnO H.O is not ppd, as it is soluble in NH.Aq. but this solution rapidly absorbs O from the air, and after a time all the Mn is ppd as hydrates of Mn,O, The presence of NH, salts hinders the oxidation process, solutions of double NH, Mn salts are scarcely changed in air if free NH, is absent Thomsen gives the thermal data $[Mn,O,H^2O] = 94,770$, $[MnO^2H^2,O] = [MnO^2H^2,H^2SO^4Aq] = 26,480$ (Th. 8, 271) $[MnO^2H^2,O] = 21,560$

MANGANO MANGANIC OXIDE, Mn.O. (Red oxide

of manganese)

Occurrence -As hausmannite, in small brownish black tetragonal forms, a c = 1 1 1537, 8G 48

Preparation -1 Pure MnCl2Aq is ppd by Na₂CO₃Aq, the pp is thoroughly washed, dried, and then heated to whiteness for some time until the weight is constant (cf Wright a Luff, C J 33, 520, with Reissig, A 103 27) —2 By strongly heating MnC₂O₄ in air (Lassaigne, A Ch [3] 40, 829) —3 Crystals of hausmannite were obtained by Debray by strongly heating a mixture of MinSO, and K2SO, in a Pt crucible (C R 52 985), also by passing a very slow stream of HCl over amorphous Mn₂O₄ heated to redness (Deville, C R '53, 199), also by keeping molten MnCl₂ in an atmosphere laden with moisture (Gorgeu, C R 96, 1044), also by melting amorphous Mn₂O₄ with borax (Nordenskjold, P 114, 112, v. also Debray, Ann M [5] 1, 124, Sidot, C R 69, 201, v Hauer, J pr 63, 425, Ebell, D P J 220, 64, 155)

It is generally stated that Mn₂O₄ is produced by heating any of the other oxides of Mn to red ness in air, according to the experiments of Dittmar (C J 1864 294) the composition of the product of heating MnO₂ in a mixture of O and N varies according to the pressure of the O, if the pressure of the O is about 19 atmos the product is approximately Mn₃O₄, while if the pressure of the O is greater than about 26 atmos the product approximates more or less closely to Mn₂O₅. The experiments of Wright and Luff (C J 33, 520), on the effect of heating MnCO₅ in air, showed that unless the heating is continued for a long time and the temperature is kept very high the product contains more O than Mn₃O₄. According to Gorgeu (C R 106, 743), finely powdered Mn₃O₄ can be oxidised to xMnO₂ yMnO, finally to Mn₂O₅, by heating in air

Properties and Reactions—A reddish brown solid powder, crystalline Mn₂O₂ is brown S G crystalline 4 856, amorphous 4 918 Mn₂O₄ is not changed when heated to a very high temperature It is reduced to MnO by H, CO, and C (Bell, C N 23, 258, Muller, P 136, 160), reduction by CO begins at c 100°, by H at c 240°, and by C at c 420° (Wright a Luff, C J 33, 520) Mn₂O, with cone H₂SO, forms a solution containing MnSO₄ and Mn₂(SO₄)₂, when the acid is hot, only MnSO₄ is formed and O is evolved With boiling HNO₃Aq, Mn(NO₃)₂ and MnO₂ are produced Hot cone HClAq produces MnCl₂ and evolves Cl Fused with alkalis, alkaline manganate is formed Cl in presence of an al kaline solution reduces an alkaline permanganate The reactions of Mn₃O₄ with acids, KlAq, &c, suggest the constitution 2MnO MnO₂ (Pickering, C J 35, 657)

HYDRATES OF. MANGANO - MANGANIC OXIDE, $Mn_2O_4xH_2O$ Such hydrates appear to exist, but their composition values Gorgeu (C R 84, 177) says a yellowish green hydrate is formed by shaking an aqueous solution of a manganese salt with alkali in presence of air Hydrates of Mn_sO₄ are also said to be formed by placing finely-powdered MnO₂ in excess of an ammonasal solution of MnCl₂ and heating (cf J Otto, A 93, 372) Veley (C J 41, 63) obtained a substance nearly agreeing in composition with $8Mn_9O_43H_2O_7$ formula by heating xMnO₂ yMnO xH₂O in H to 200°

Manganic oxide, Mn₂O₃ (Sesquioxide of manganese)

Occurrence —As braunte in quadratic octahedra, S G 4 752 (Rammelsberg, P 124, 513) The hydrate Mn₂O₃ H₂O occurs native as mangamts

Preparation -1 The pp-approximately MnO_2xH_2O —obtained by passing Cl into Na_2CO_3Aq holding finely powdered MnCO₃ in suspension, is made into a thin cream with sone H_2SO_4 and slowly heated on an oil bath to 100° , at which temperature O is suddenly evolved, and the mass becomes thicker and

greyish violet in colour, it is then heated to 138° until it is dark green. The impure Mn₂(SO₄), thus produced is placed on a warm porous plate, by which H₂SO, is absorbed, it is then rubbed with conc HNO, Aq, free from HNO2, again dried on a porous tile, and then warmed to 130° The Mn₂(SO₄), thus produced is exposed to air, when it rapidly deliquences to form a violet solution, which afterwards becomes turbid from separation of Mn₂O₃.H₂O $(Mn_2(SO_4)_3 + 4H_2O = Mn_2O_3 H_2O + 3H_2SO_4)$ The brown solid which separates is washed, dried at 100° and then gently heated until the water is removed (Carius, A 98, 53)—2 According to Schreider (P 107, 605), Mn₂O₄ is obtained by heating MnO₂, MnO, or Mn₂O₄ in O (but v. account of Dittmar's experiments under Mangano manganic oxide, supra) Moissan says that artificially prepared MnO₂ goes to Mn O₃ when heated in O to 250° (A Ch [5] 21, 232) According to Berthelot (A Ch [5] 15, 185) and Knab, Mn₂O₂ is obtained by heating MnCl₂, MnBr₂, or MnI₂ in air or O This oxide is also said to be formed, with evolution of O, by passing H₂O vapour over heated K MnO₄ Gorgeu (C R 108, 1106) obtained Mn O₃ by allowing ppd MnCO, to remain in contact with aerated water for 10 years, also by exposing MnO H2O to O in presence of excess of a man ganous salt, also by exposing solutions of MnSO₄, MnCl₂, and Mn(C₂H₄O₂)₂ to sunlight Properties and Reactions—A black powder,

Properties and Reactions—A black powder, S G 4325, the mineral braunite forms brownish black, very hard, lustrous quadiatic octahedra, S G 4752 Deoxidised at white heat to Mn₂O₄ Soluble in conc H₂SO₄, forming a reddish liquid, which evolves O on warming, and then contains MnSO₄, boiled with dilute H₂SO₄Aq or HNO₃Aq, MnO₆ is separated, and manganous sulphate or nitrate goes into solution (Christensen, J pr [2] 28, 1) Soluble in cold conc HClAq, forming a brown liquid, which most probably contains Mn Cl₅ (v Manganic chloride, p 180)

Mn₂O₃ is a basic oxide, the corresponding salts are not numerous, they are readily reduced to manganous salts Mn (SO₄)₃ combines with alkali sulphates to form alums Mn₂O₁ leacts with hot HClAq, with KIAq, and other reagents, as if it were MnO MnO₂ (Pickering, C J 35, 657) Laugier (C R 104, 1508) describes several compounds of Mn₂O₃ with SeO₃, prepared by the reaction of MnO₂ with H₂SeO₃Aq

Hydrate of manganic oxide, Mn.O., H₂O Occurs native as manganite, S G 4 335, iso morphous with göthite and diaspore, the corresponding Fe and Al compounds The preparation of Mn₂O₃ H₂O is described under Mangania oxide (v supra), it forms a brownish black powder Warmed with cone H₂SO₄ to c 100°, Mn₂(SO₄), is formed without evolution of O (Carius, A 98, 53) According to Carius (le), Mn₂O₄ H₂O is not dissolved by dilute H₂SO₄Aq even on gently warming, but if a little MnO is present solution occurs in the cold Mn₂O₄H₂O is said by Hermann (P 74, 303) to dissolve in tartaric acid, forming a brownish red liquid, from which manganous tartrate separates on standing, the liquid becoming colourless and now containing formic acid and CO₂ In a stream of H₂S₄ a little MnSO₄ and also MnS

and Mn₂O₂ are formed (Wagner, D P J 195, When moist Mn₂O₂ H₂O is shaken with magnesia alba, K.CO3, or Na.CO3, or even with water, and much air, nitrates are produced according to Reichardt (Henneberg's J für Landwirthsch 26, 167)

MANGANESE PEROXIDE, MpO2 (Manganese

dioxide)

Occurrence - As pyrolusite, in iron black, opaque, rather brittle trimetric crystals, a b c = 776 1 1 066, SG 4 82 to 4 97 The name is supposed to have been given from the use of the mineral to remove the colour from glass: coloured by compounds of iron $(\pi \hat{v} \rho = \text{fire}, \text{ and }$ Aveir = wash out)

Preparation - Pure MnCO3 is dissolved in as small a quantity as possible of dilute HNO, Aq, the solution is evaporated to a syrup, which is heated to 160°-165° for some hours, the product is thoroughly washed with boiling water, then dried over H.SO4, and heated to c $180^{\circ}-200^{\circ}$, until every trace of water is ie moved Pure MnO. is thus obtained, exactly resembling pyrolusite (Gorgeu, C R 88, 796, Wiight a Menke, C J 37, 45, cf Schlösing, C R 55, 284, and Kuhlmann, D P J 211, 25) Even it the Mn(NO₃)₂ used contain a large quantity of KNO₃, MnO₂ practically free from K₂O is obtained by this method

Very many attempts have been made to obtain pure MnO, by ppn from Mn salts, eg by ppg with BrAq in presence of Na acetate, by passing Cl into an alkaline solution containing MnCOs in suspension, by reacting on a Mn salt solution with KMnO, Aq, &c The various methods have been examined by Gorgeu (C R 88, 796, A Ch [3] 66, 153), Guyard (Bl [2] 1, 89), Hannay (C J 33, 269, cf Beilstein a Jawein, B 12 1530), Pickering (C J 35, 654), Volhard (A 198, 318), Kessler (T) 18, part 1), Pattinson (C J 35, 365), Veley (C J 37, 581), Wright a Luff (C J 33, 504), and Wright a Menke (C J 37, 22) The outcome of the work is that pure MnO, cannot be obtained by any of the ppn methods, either the pp is x MnO y MnO, or, if all the Mn is present as MnO, the pp contains also K O or some other base besides H,O Volhard's method-adding excess of kMnO₄Aq to MnSO₄Aq in presence of HNO3 (exact quantities are given by V)—gave all the Mn as MnO accompanied by a small quantity of KO (c 3 pc), which could not be removed by washing (W a M, lc)

Properties -A black, or brownish black, hard, crystalline powder SG 502 Heated to moderate redness, Mn.O, is formed, heated to whiteness, Mn₃O, remains (cf Heated Mangano manganic oxide, Preparation, 182) MnO. is a conductor of electricity, it is Reacts strongly electro negative to the metals with acids to form salts corresponding with MnO, with cold cone HClAq most probably

forms Mn Cl.

Reactions —1 Heated, gives Mn₂O₃ at moderate redness, and Mn₃O₄ at white heat —

8 Heated in hydrogen, or carbon monoxide, is reduced to MnO, reduction in H begins at c 190°, and in CO at c 87°, when heated with carbon reduction begins at c 390° (Wright a Luff, CJ 38, 518) -3 Heated with polassium chlorate, O is evolved and MnO₂ and KCl remain: KnO 2 when 2 with a reducing agent such as SO₂, carbon reduction begins at c 390° (Wright a Luff, CJ 38, 518) -3 Heated with polassium in combination with MnO₂, but that the ratio of chlorate, O is evolved and MnO₂ and KCl remain: KnO 20 when 20 with a reducing agent such as SO₂, carbon reduction begins at c 390° (Wright a choice of the color o

a little Cl is evolved, and at one stage of the change KMnO, is produced. The reaction between MnO, and KClO, probably produces KMnO, Cl, and O, the KMnO, then decomposes to K_2MnO_4 , MnO_2 , and O, and the K_2MnO_4 reacts with Cl to form KCl, MnO2, and O The following equations are given by McLeod as expressing approximately the various changes: (1) $2MnO_2 + 2KClO_3 = 2KMnO_4 + Cl_2 + O_2$,

(2) $2KMnO_4 = K_2MnO_4 + MnO_2 + O_2$, (2) $\Sigma_{NM10} = N_{1M10} + M_{10} + M_{10} + V_{2}$, (3) $K_{2}M10 + Cl_{2} = 2KCl + M_{10} + C_{2}$ (v McLeod, C J 55, 184, Hodgkinson a Lowndes, C N 59, 63, Fowler a Grant, C J 57, 272, Baudimont, J Ph [4] 14, 84, 161, Warren, C N 58, 247, Veley, T 1888 [1], 271, Spring a. Prost, 1898 [1], 271, Spring a. Prost, 1888 [1], 271, Spring a. Prost, 18 Bl 1889 340) -4 With hot conc sulphuric acid, MnSO, is formed and O evolved -5 With cold cone hydrochloric acid, Mn₂Cl₂ is very probably produced, on warming, Cl is evolved and MnCl, remains (cf Manganic chloride, p 180) —6 Heated with sulphuric acid and oxidisable bodies, MnO acts as an oxidiser, $e g H_2C_2O_4$ is thus oxidised to CO_2 and H_2O -7 Not acted on by moderately dilute nitric acid alone, but in presence of an oxidisable body, Mn(NO₃)₂ and oxidised products are formed, e.g. with HNO, and HCl, Clis evolved -8 Compounds of Mn O, with SeO, were obtained by Laugier (C R 104, 1508), by heating ppd MnO₂ with selenious and -9 With hydrogen peroxide and an acid, forms a salt of MnO and H2O and evolves O, with hydrogen peroxide alone, O is evolved and the same quantity of MnO₂ remains as was originally used (v Hydrogen Peroxide. Reactions 11 and 19, vol 11 pp 723, 724) -10 Heated with magnesium chloride, MnCl, and MgO are formed and Cl is evolved -11 Fused with alkalis in presence of air or oxygen, manganates Mi MnO, are formed (v Manganates under Manganese, oxyacids of, p 185)

12 MnO₂ combines with a number of basic orides to form salts of the form aMO yMnO, known as manganites According to Gorgeu (A Ch [3] 66, 153) MnO, decomposes neutral solutions of many salts of Ca, Ba, Ag, and Mn, making the solutions acid to litmus and combining with the bases From dilute solutions of K2CO. and Na CO₂ MnO₂ withdraws and combines with 7 pc K₂O, and 41 pc Na₂O, respectively, according to Gorgen, the manganites thus produced approximately correspond with the formula M₂O 15MnO₂ According to Jolles (Chem. Zeitung, 11, 1394) K₂MnO₃ is obtained, as a brown yellow solid, by mixing equivalent quantities of K VinO, and C.H.O Wright and Menke (C J 37, 22) have examined the potassium manqanites formed by ppg MnO₂ in presence of K salts, by passing Cl into K₂CO₂Aq holding MnCO, in suspension, by adding MnSO, Aq to KMnO,Aq, &c , they conclude that the amount of K₂O ppd in combination with MnO₂ varies according to the relative masses of the reacting bodies, the temperature, the quantity of free acid present, &c, and that it tends to the maximum 5M3O2 K2O W a M failed to obtain 5MyO, K.O W a M failed to obtain 8MnO, K.O 3H,O described by Stingl a Morawski (J pr [2] 18, 91) as produced by acting on 109) gave the formulæ CaO MnO, and CaO 2MnO, to the manganutes formed by oxidising MnO H₂O by air in presence of lime Manganutes of the form MO 5MnO,, where M = Ca, Ba, Sr, Zn, and Pb, are described by Risler (Bl [2] 30, 110) as produced by heating KMnO, with slight excess of various metallic chlorides, and washing with water By heating metallic chlorides with MnO, and then adding MnCl, Rousseau obtained manganutes, which he classes as MO 5MnO, MO MnO, and 2MO MnO, (C R 101, 167, cf also Post, B 12, 1484, 1537, Rammelsberg, B S, 233, Rousseau, C R 102, 425, 615, 103, 261, 104, 786, 1796) Various compounds of MnO with MnO, seem to exist, these may be regarded as manganese manganutes, v Oxides intermediate between manganuc oxide and manganese percarde. wifra

oxide, mira13 While MnO₂ reacts as an acidic oxide towards the oxides of the more positive metals, it also reacts as a basic oxide with some acids. The usual reactions of MnO₂ with acids are those of a basic peroxide (v Reactions, 3 to 6, supra). The salt MnO₂ SO₃ is said by Fremy to be formed by carefully reacting on MnO₂ xH₂O with cone H.SO₄, and allowing to stand in air (C R 82, 475). By adding MnSO₄ to a freshly prepared solution of Pb₂O₄ in acetic acid, as long as PbSO₄ was ppd, Schönbein (J pr 74, 325) obtained a deep brownish red liquid, which had strongly oxidising properties, and from which MnO₂ separated on standing, or more quickly on boiling. Schönbein thought that this liquid contained an acetate of MnO₂, but he did not succeed in isolating this salt.

HYDRATES OF MANGANESE PEROXIDE approximately pure MnO2 is ppd, by oxidising manganous salts in alkaline solutions, or by re actions between manganous salts and permanganates, or by decomposing KMnO, Aq by H SO, or HNOs, the pp always contains water, but it is very doubtful whether any definite, and fairly stable, hydrate of MnO₂ exists When the process of formation results in ppn of all the Mn as MnO_2 the composition of the pp approximates to MnO_2 H₂O, but this body loses water in dry air (v Wright a Menke, C J 37, 22) When the whole of the Mn is not ppd as MnO2, the pp consists of compounds of the form xMnO2.yMnO zH2O containing variable quantities of metallic oxides according to the conditions of formation It appears to be possible to obtain hydrates which are stable for many hours within definite limits of temperature, but these hydrates are of the form $xMnO_2yMnOsH_2O$ (v Veley, C J 37, 581, 41, 56)

References — The following papers contain the chief experiments bearing on the formation and composition of supposed hydrates of MnO — Rammelsberg, B 8, 233, Fremy, C R 82, 1231, Van Bemmelen, B 13, 1466, Gorgen, A Ch [3] 66, 154, C R 108, 948, Von Hauer, W A B 13, 453, Reisig, A 103, 206, Böttcher, J pr 76, 235, Guyard, Bl 6, 81, Morawski a Stingl, J pr [2] 18, 90, 97, Volhard, A 198, 318, Suckow, D P J 177, 231; Wernicke, P 141, 116, Veley, C J 37, 581, 41, 56, Pickering, C J 35, 654, Wright a Luff, C J 33, 504, Wrighta Menke, C J 37, 22, Franke, J pr [2] 36, 166, 451

OKIDES INTERMEDIATE BETWEEN MANGANIC

OXIDE AND MANGANESE PEROXIDE These oxides belong to the general formula xMnO yMnO The composition of the pp obtained by adding water to solutions of MnO or Mn₂O₃ in cold cone HClAq varies between 16MnO₂5MnO and 36MnO₂5MnO (Pickering, C J d5, 659) By passing Cl for a limited time into solution of Mn acetate, Veley obtained a pp approxi mating in composition to 5MnO, MnO xH,O (C J 37, 581, 41, 56,, by heating this pp in a current of air, the compound 11MnO MnO H2O was produced, and by heating the first compound in O, the body produced had the composition 23MnO₂MnO₂H₂O Wiight a Menke (C J 37, 22) obtained a number of bodies xMnO₂ yMnO xH₂O by various processes of oxi dising manganous salts, and reducing permanganates, in every case, however, KO, or other alkalı, was held in combination Further ac counts of these intermediate oxides, many of which were probably mixtures of the better de fined oxides of Mn, will be found in the memoirs referred to under Hadrates of Manganese per OXIDE (v supra), especially in the memoirs of Gorgeu

MANGANFSE TRIONIDE, MnO, This compound is formed, in very small quantities, by slowly dropping a solution of KMnO, in cold conc H₂SO₄ (c f grams KMnO₁ in 100 cc H SO₄) on to dry Na₂CO₃ The Na CO₃ is placed in a dis tilling flask surrounded by cold water The flask is connected with a U tube filled with fragments of glass, and surrounded by a mixture of ice and salt, and this tube is connected with another \bigcup tube containing a little dilute H_2SO_4Aq As each drop of the green solution of $KMnO_4$ in H_2SO_4 falls on to the Na CO_3 , a pink cloud is formed, the cloud partly condenses in the first U tube, and part of it passes on and is dissolved in the HSO, in the second tube (Franke, C J [2] 36, 31, 166, v also Thorpe a Hambly, C J 53, 175) Only a very small Only a very small quantity of MnO₃ can be obtained It appears as a reddish, amorphous, deliquescent mass slowly decomposes at ordinary temperatures, but is fairly stable if surrounded by ice and salt (T a H, l c) MnO₃ is decomposed by water yielding HMnO, Aq and MnO, (T a H), according to Franke, H.MnO, is produced, but quickly decomposes to MnO₂, O, and HMnO, and probably also H Mn₂O, MnO, dissolves in conc H SO4, forming a green solution Franke thinks this liquid contains (MnO,) SO, MnO, dissolves in KOHAq, forming K2MnO liberates I from KI, and acts on Hg similarly to ozone (T a H)

Manganese hpproxide, Mn₂O₇ (Permanganic anhydride) This oxide was obtained by Thenard (C R 42,382) Its composition was determined by Aschoff (J pr 81, 34) Pure KinO₁, free from Cl compounds, is added little by little to cone H SO₄, S G 1 845, kept cold by a freezing mix ture. To the green solution thus obtained a few drops of water are added, when Mn₂O₇ slowly separates in dark redaish-brown oily drops. If acid of the composition H₂SO₄ HO (S G c 1 78) is used, oily drops of Mn₂O₇ are formed without addition of water. According to Franke (J pr. [2] 36, 31), a solution of KMnO₄ in cone H₂SO₄ contains (MnO₂)₂SO₄, and this is decomposed by a little water, giving Mn₂O₇ and H₂SO₄.

Terreil (Bl 1862 40) prepares Mn₂O, by dissolving KMnO₄ in well cooled H₂SO₄, con taining water in the ratio H_2SO_4 $\frac{1}{2}H_2O$, placed in a stoppered retort, the beak of which passes into a glass balloon surrounded by a freezing mix-Corks or organic material must not be used in any part of the apparatus He heats the retort to 60°-65° (not over 70°), when purple red vapour is evolved and condensed to a thick greenish black liquid, which is Mn,O Only a few drops of Mn₂O, can thus be prepared at a time As soon as a certain quantity collects in the balloon, decomposition occurs, with slight

detonation (v also Spiess, J pr [2] 1, 421)
P Thenard (J pr 69, 58) describes Mn₂O, as a dark olive green liquid, with a smell recalling Cl compounds and ozone Ascholf (J pr 81, 34) describes it as dark brownish red oily drops, which do not solidify at -20° Mn₂O, slowly decomposes in air at ordinary temperatures, with evolution of O It may be heated to 60° - 65° , under reduced pressure, without vola tilising, at a somewhat higher temperature it is suddenly and violently decomposed to MnO2 and O Mn O, is very hygroscopic It dissolves in water to form a puiple liquid, probably containing HVnO. This liquid is slowly decomposed on warming into MnO2 and O Mn O, dissolves in cold conc H SO4, appare tly with out decomposition, to form an olive green liquid (this liquid contains (MnO₃)₂SO₄ according to Franke, J pr [2] 30, 31) Mn O, is at once de composed by contact with small quantities of MnO_2 , Ag O, or HgO (Aschoft, l c) Mn O, 18 a powerful oxidiser It inflames paper or alcohol.

MANGANESE TETROXIDE (?) Franke (J pr [2] 36, 31, 166) states that a blue gas is obtained by leading air or CO, saturated with water at $40^{\circ}-50^{\circ}$, over the green liquid formed by dissolving KMnO, in well cooled conc H2SO, this blue gas he gives the formula MnO. Thorpe and Hambly repeated Franke's experiments (C J 53, 178), but failed to obtain any indications

of the formation of a blue gas

Manganese, oxyacids of, and their salts Two series of salts derived from oxyacids of Mn are known—the manganates Mi2MnO, and the permanganates M'MnO, The and corresponding to the manganates, viz H₂MnO, has not been isolated, but its anhydride MnO, is known The anhydride of permanganic acid, viz Mn.O. is known, and the acid itself has also probably been isolated

MANGANATES, M, MnO, derived from the hypothetical acid H2MnO4 The anhydride of this acid, viz MnO, is known A solution of this oxide ip water perhaps contains H2MnO4, but it decomposes almost at once to HMnO, and MnO, (v Manganese trioxide, p 184) an acid is added to solution of a manganate, the manganic acid produced at once decomposes to permanganic acid and MnO₂. This change occurs even when CO2 is passed into solution of a manganate The manganates are isomorphous with the sulphates

The fact that the product of fusing together pyrolusite, potash, and saltpetre dissolved in water to form a green liquid, which became blue, violet, and then red, on addition of much water, was known to Scheele To the green substance Scheele gave the name 'Chamaleon minerale.'

Chevillot and Edwards, in 1817, showed that the green substance was a definite compound of potash with an acid of Mn (A Ch [2] 4, 287, 8, 337) Forchhammer (Annals of Phil 16, 310, 17, 150) and Fromherz (P 31, 677) investigated the manganates Mitscherlich, in 1830, showed that two salts are obtained by the action of alkali on pyrolusite in presence of air or alkali nitrate (P 25, 287)

Manganates of the alkalis and alkaline

earths are obtained by heating MnO2 with KOH, CaO₂H₂, &c, to c 150° in absence of air, or to higher temperatures in presence of air, or by strongly heating any Mn salt with KOH, CaO.H., &c, in presence of O or an oxidiser, eg KClO. K.MnO. and Na.MnO. dissolve with out decomposition in water containing alkali In pure water, KMnO, or NaMnO, is formed and MnO₂ ppd Solutions of the alkali manganates are decolourised, with ppn of MnO_2 , by easily oxidised bodies, eg SO Aq, As O_3 Aq, H_2 SAq, or ferrous salts Ba and Sr manganates are in soluble in water

Barrum manganate BaMnO, A dark green powder SG 485 Insol water Unchanged in air, decomposed by acids pared by calcining Ba(NO₃)₂ with MnO₂, or by projecting finely powdered MnO₂ into a molten mixture of KClO, and BaO, H2, washing with hot water, and drying By heating MnO₂ with Ba(NO₃), BaMnO₄ is obtained as a green powder consisting of minute hexagonal crystals (Forch hammer, Annals of Phil 16, 130, 17, 150, Rosenstiehl, J Ph 46, 544, Schafavik, J pr The salt is also obtained by digesting Ba(MnO4)2 with BaOAq

Didymium manganate Di. (MnO4)3 black powder, insol water Obtained by heating for 30 minutes 1 pt MnO with 4 pts Di3NO. and washing with water (Frerichs a Smith, A

191, 353)

Lanthanum manganate La. (MnO.), Resembles the Di salt, prepared similarly (F a. S lc)

Potassium manganate K.MnO.
Formation —1 A mixture of equal parts of

finely powdered MnO2 and KOH is heated to bright redness in air, or in O, 3MnO2+2KOH $= \bar{K}_2 MnO_4 + Mn_2O_3 + H_2O \quad K \quad MnO_4 \text{ is formed by}$ heating MnO, and KOH in absence of O to c 150° (Beketoff, Bl 1, 43), the reaction occurs in N at c 180° (Elliot a Storer, P Am A 5, 192) If the mixture is heated above 180° O must be present, because at c 190° K2MnO4 is decomposed with reformation of MnO₂—
2 By boiling cone KMnO₄Aq with KOHAq; 2KMnO,Aq + 2KOHAq = 2K MnO,Aq + \mathbf{H} ,O + $\hat{\mathbf{O}}$ (Aschoff, J pr 81, 29) According to Thenard (J pr 69, 58), this reaction only occurs when the KOH contains some oxidisable substances, eg a little organic matter —3 By long continued heating KMnO, to 240°

 $2KMnO_4 = KMnO_4 + MnO_2 + O_2$ (Thenard, lc) 4 By fusing any oxide of Mn with KOH in presence of O, or an oxidiser such as KClO,

Preparation -2 pts KOH are dissolved in the smallest quantity of water, 1 pt KClO, and 2 pts very finely powdered MnO2 are added, the mi ture is dried, and then heated, nearly to redness, for a long time in a Pt dish, the fused mass when cold is treated with a little water, the conc green solution is decanted, after standing until quite clear, and evaporated in vacuo

over H2SO.

Properties and Reactions - Dark green crystals, isomorphous with K.SO, and K.CrO, Soluble in water containing KOH without decomposition, dissolves in pure water with decomposition to KMnO₄Aq and MnO₂ Dilute acids, even CO2, quickly decompose K2MnO4, forming K permanganate and a manganous salt, e q with H.SO₄, —5K₂MnO₄Aq +4H₂SO₄Aq =2K₂Mn.O₆Aq + MnSO₄Aq +3K₂SO₄Aq +4H.O Heated in CS₂, MnS, CO₃, and polysulphides of K are formed (Muller, P 127, 404) Heated in a stream of water vapour, Mn₂O₅, KOH, and O are produced

 $(2K_a \text{MnO}_4 + 2H_2O = \text{Mn}_2O_3 + 4KOH + 3O)$ fusing MnO2 with KOH in air, and then passing water vapour over the product, then again fusing the products together, and repeating these processes, O may be obtained from the atmosphere

Sodium manganate Na2MnO, 10H2O Obtained by long continued heating equal pts finely powdered MnO2 and NaNO3, boiling with water, filtering, and allowing to cool (Gentele, J pr 82, 58) Said to form colourless crystals, resembling Glauber's salt, and to dissolve in water with partial decomposition to form a green solution

PERMANGANIC ACID and PERMANGANATES acid HMnO4, or H2Mn2O8, has probably been isolated, a series of salts derived from this acid is known Permanganic anhydride, Mn₂O₂, is a very unstable liquid, it dissolves in water to form HMnO,Aq, which slowly decomposes to MnO₂ and O Permanganic acid and its salts readily part with O, and hence act as energetic oxidisers The permanganates are isomorphous with the perchlorates M'ClO₄, they are purple red, all are soluble in water, the least soluble is the Ag salt These salts are produced by the action of dilute acids, or of Cl, on the man ganates, or by the reaction of several oxidisers, e q Pb₃O₄ and dilute HNO₃Aq, on Mn salts — (Tamm, J 1872 910, Fresenius, Fr 11, 415, 425, Crum, A 60, 219, Gibbs, Am S [2] 14, 204, Chatard, C N 24, 196, Pichard, C R 75, 1981 Colored R 18 (1981) Pichard, C R 75, 1981 Colored R 18 (1981) Pichard, C R 75, 1981 Colored R 18 (1981) Pichard, C R 75, 1981 Colored R 18 (1981) Pichard R 18 (1981 1821, Deshayes, Bl [2] 29, 541, Volhard, A 198, 354, Rose, P 105, 289) KMnO is reduced to K,MnO by boiling cone KMnO, Aq with potash (cf. Potassium Manganate, Formation No 2, p 185) Solutions of permanganates are decomposed by NH₃Aq with separation of xMnO2 yMnO, they are reduced to manganous salts by HNO₃Aq, fairly cone HClAq, SO₂Aq, Na.S.O.Aq, many organic compounds, &c H.SO.4 decomposes solid permanganates with separation of MnO, and evolution of O tions of HMnO4 and KMnO4 absorb the green and yellow green rays of the spectrum, the absorption spectrum has been examined by Lecoq de Boisbaudran (Spectres lumineux, p According to Vogel (B 8, 1534) $\frac{1}{250000}$ pt of Mn may be detected, in presence of Cu and Fe compounds, by boiling with PoO2 or Pb,O4 and dilute HNO,Aq free from Cl com pounds, and examining the absorption spectrum of the solution (of permanganate) produced

Ammonium permanganate NH, MiO,. Resembles KMnO, with which it is isomorphous, v sol water, decomposed by gently

heating Prepared by rubbing together AgMnO. and NH, ClAq in the ratio AgMnO, NH, Cl, filtering, and evaporating at the ordinary temperature over H₂SO₄, also by decomposing BaMnO₄ by (NH₂)₂SO₄ (Böttger, N R P 25, 115)

Barium permanganate BaMnO, Small, hard, rhombic ontahedra, almost black, with violet sheen Prepared by adding excess of violet sheen Prepared by adding excess of H₂SiF₆Aq to KMnO₄Aq, filtering from K SiF₆ through asbestos, saturating with BaOAq containing BaO2H2 in suspension (BaCO2 should not be used as it causes ppn of MnO₂ xH O), decanting from $BaSiF_{e}$, and ϵ /aporating (Rousseau a Bruneau, C R 93, 229) Böttger (N R P 25, 115) prepares BaMnO, by dissolving in water the product of the fusion of 2 pts KOH and 1 pt MnO₂, filtering, and adding BaCl₂Aq until the green colour of the liquid disappears, he collects the violet blue pp , and washes it with cold water till the washings begin to appear reddish, he heats this pp, which is Ba(MnO4), with water, passes in CO2 till the liquid is purple red, filters from MnO₂, and evaporates

Calcium permanganate CaMnO, 5H2O A crystalline, deliquescent mass, prepared by decomposing AgMnO₄ by CaCl₂Aq, following directions given for obtaining NH₄MnO₄ (v

Cobast permanganate does not seem to have been isolated, but Klobb has prepared several luteo cobaltic permanganates, viz Co2(NH3)12(MnO4)6, $Co (NH_3)_{12}Cl_4(MnO_4)$, $Co_2(NH_3)_{12}Br_4(MnO_4)_2$ (C R 103, 384, Bl [2] 48, 240)

Potassium permanganate KMnO, Formation -1 By fusing together KOH and an oxide of Mn in the air or with KClO3, dis solving the K2MnO4 in water, passing in CO2 filtering from MnO2, and evaporating

 $(3K_2MnO_4Aq + 2CO_2 = 2KMnO_4Aq + 2K_2CO_3Aq + MnO_2) - 2$ By warming solution of a Mn salt with KCO, and KClOAq -3 By melting MnO, with kHO, making a conc solution of the fused mass, adding saturated MgSO,Aq, and filtering

 $\begin{array}{l} (3 \text{K}_2 \text{MnO}_4 \text{Aq} + 2 \text{MgSO}_4 \text{Aq} \\ = 2 \text{KMnO}_4 \text{Aq} + 2 \text{K}_2 \text{SO}_4 \text{Aq} + 2 \text{MgO} + \text{MnO}_2) \\ (\text{Tessié du Mothay}, \ D \ P \ J \ 186, 231) - 4 \ \ \text{By} \end{array}$ passing Cl into a solution of the fused mass ob tained as in 1 and 3, and evaporating (Stadeler, $J pr 103, 107) (2K_2MnO_1Aq + Cl)$

 $=2KClAq + 2KMnO_{\bullet}Aq)$

Preparation -A mixture of 2 pts KOH and 1 pt KClO₃ is melted in a thin sheet iron crucible, the crucible is removed from the lamp, and 2 pts very finely powdered and sifted MnO, are added, little by little, heating is then continued, with stirring, until the mass gets quite hard, the temperature is then raised for a short time to full redness, when cold, the mass is broken up, and boiled with so much water that no crystals separate on cooling (c 40 pts water for 1 pt KClO, used), a rapid stream of well washed CO2 is passed into the boiling liquid until a drop placed on paper makes a red stain (showing no green at the edges), the outer part of which soon becomes brown After cooling the greater part of the liquid is poured off, the rest is filtered (from MnO) through glass wool. and the whole is evaporated until a drop placed on a cold surface quickly deposits crystals. After standing 12 to 24 hours the greater part of the KMnO₄ separates out, a little is obtained by further evaporating the mother liquor 100 grms pyrolusite give about 30 grms KMnO₄ (Böttger, J pr 90, 156, for modification of this method, v Grager, J pr 96, 169, Wöhler, P 27, 626, Gregory, J Ph 21, 312, Mitscherlich, P 25, 287, Elliot a Storer, P Am A 5, 192) Béchamp (A Ch [3] 57, 293) heats MnO₂ with KOH, and oxidises by passing O over the fused mass, he then dissolves in water, passes in CO₂, and evaporates

Properties — Dark purple red, almost black, rhombic crystals, a bc = 79523 1 6478 S G 2 71 (Kopp) Isomorphous with KClO, S at 15° = 6 25 (Mitscherlich) Decomposed by heat, giving K,MnO, and O Pure conc KMnO, Aq can be boiled without change, in presence of oxidisable bodies KMnO, Aq is quickly reduced Reactions—1 Heated to 240°, MnO, K,MnO,

and O are produced (Chevillot a. Edwards, A Ch [2] 4, 290) At higher temperatures xMnO yk O is formed (Rousseau, $C \hat{R}$ 104, 786) -2 Sulphunc or nitric acid separates HMnO, which decomposes with evolution of O and ppn of MnO2, Mn2O3, or xMnO2yMnO, with consider able excess of warm H2SO, Aq or HNO, Aq, MnSO, or Mn(NO₃) is produced Cold cone H SO₄ dis solves kMnO, forming a green liquid, from which a few drops of water cause separation of Mn O, (cf Manganese heptoxide, p 184, v also Manganese trioxide, p 184) —3 Hydrochloric acid in excess forms MnCl, and evolves Cl Dry HClevolves Cl, and forms H_aO , hCl, $Mn_2O_3xH_2O$, MnCl., and probably Mn.Cl. (Thomas, C J 33, 372) -4 Sulphunc acid and oxidisable bodies either separate MnO, or vMnO, yMnO, the oxidisable body being simultaneously oxi dised, or if there be enough acid to prevent ppn of xMnO₂yMnO, MnSO₄ is formed With H₂CO₄ and H₂SO₄, CO₂ and HO (besides K₂SO₄ and MnSO₄) are produced (of Berthelot, A Ch [5] 21, 176, Harcourt, C J [2] 5, 460, Jones, C J 33, 95)Harcourt (lc) represents the re action thus

 $2kMnO_1Aq + 3HSO_1Aq + 5H_2C_1O_1Aq$ $= K SO_4 Aq + 2 MnSO_4 Aq + 10CO_2 + 8H O$ Jones (lc) says that HO, KCO, and MnCO, are at first produced on adding KMnO,Aq to HCO,Aq, and that further addition of KMnO,Aq forms KCO, ppts Mn₂O, and evolves CO, and O Alcohol gives Kacetate and a pp containing MnO2, MnO, and K.O, glycerin gives a similar pp and forms K.CO2 (Morawski a Stingl, J pr [2] 18, 78, cf Berthelot, lc)—
5 According to Aschoff (J pr 81, 29) cone
KMnO₄Aq is reduced to K.MnO₄ by boiling with potash solution (2KMnO,Aq+2KOHAq = $2K_2MnO_4Aq + HO + O$, Thenard (J pr 69, 58) says that this action does not occur unless traces of oxidisable substances, e.g. organic matter, are present—6 kMnO₄Aq acidified by H2SO, reacts with hydrogen peroxide to form H₂O, O, and MnSO. At low temperatures, c 12°, the KMnO₄ is decolourised, but O is not evolved, according to P Thenard (C R 75, 177), Berthelot (A Ch [5] 21, 176) thinks that H₂O₄ (?) is formed (v also Swiontrowski, A 141, 205, Aschoff, P 111, 217) -- 7 KMnO, Aq is decomposed with separation of MnO2, Mn2O2, or xMnO2 yMnO, by ammonia (Cloez & Guignet,

C R 47, 710, Wohler, A 136, 256, Wanklyn a Gamgee, C J [2] 6, 25, Tamm, C N 25 47), by hydrogen (Jones, C J 33, 96, Wanklyn a Cooper, P M [5] 6, 288), by phosphine, arsine, and stibine (Jones, Ic, Schobig, J pr [2] 14, 289, Parsons, C N 1877 236), by chlorine dioxide [ClO₂] (Furst, A 206, 75)—8 With potassium sulphocyanide, K₂SO₄ and KCNO are produced (Morawski a Stingl, J pr [2] 18, 78)—9 Sodium thiosulphate in boiling solution is wholly oxidised to Na₂SO₄ by fairly cone KMnO₄Aq, if the KMnO₄Aq is very dilute from to 2½ p c Na₂S₂O₃ remains (Glaser, M 7, 651) Combination—From cone mixed solutions of

Combination — From cone mixed solutions of KMnO, and K₂MnO, the salt KMnO, K.MnO, separates in small, six sided, monoclinic tablets

(Gorgeu, J pr 80, 123)

Sodium permanganate NaMnO, 3H O Formed similarly to KMnO,, or by the reaction between AgMnO, and NaClAq V sol water, and hence obtained in crystals with difficulty

Silver permanganate AgMnO, Monoclinic crystals S 91 in cold water Obtained by mixing cone warm kMnO, Aq with AgNO, Aq, and allowing to cool (Dewar a Scott, Pr. 35, 44) Klobb (C R 103, 384) obtained AgMnO, 2NH, by saturating KMnO, Aq with NH, and then adding an equivalent quantity of AgNO.

Per manganates of copper, didymium (Frenchs a Smith, A 191, 354), lanthanum (F a S, lc), lead, lithium, magnesium, strontium, and zinc,

have been isolated

Permanganic acid, HMnO, The solution obtained by decomposing powdered Ba(MnO,), by an exactly equivalent quantity of HSO,Aq, contains this acid Hunefeld (Schweiger, Jahrb der Chem und Phys 30, 133) says that the acid can be obtained, in indigo like crystals, by washing Ba(MnO,), with hot water, whereby it is decomposed to MnO and BaMnO, filtering, adding exactly enough phosphonic acid to decompose the Ba salt, heating to 60°-100°, filtering, and evaporating at a low temperature (No analyses are given)

Manganese, oxychlorides of Several oxychlorides of Vin appear to exist, but they have not been satisfactorily examined P de Saint Gilles (C R 55, 329) says that MnCl₂ 3Mn O₄ is formed as a black powder, resembling MnO₂, by heating to 280°, in a partially closed vessel a mixture of MnCl, and NaNO₃ Gorgeu (A Ch. [6] 4, 515) obtained an oxychloride, to which he provisionally assigned the formula MnCl MnO by heating MnCl₂ in water vapour According to Aschoff (J pr 81, 29) the gas which Dumas obtained by adding pieces of fused KCl or NaCl to a mixture of kMnO₄ and cone H SO₄, and which he said was MnCl₇, is probably an oxychloride having the composition MnO₂Cl

Manganese oxyfluoride of. According to Nickle's (C R 65, 107) the compounds MnOF KF and Mn₂OF₂ 2k.F are ppd, when solution of MnO₂ in ethereal HCl is poured into boiling KFAq or NaFAq Christensen (J pr [2] 30, 57), however, asserts that the double compound obtained as described above is MnOF.

Manganese, oxysulphide of The compound MnO MnS is said to be formed, by Arfvedson (P. 1, 50), by heating MnSO, in H, it is a green solid, which dissolves in acids with evolution of H_2S , heated in air it burns to Mn_2O_4

Manganese, phosphides of Several compounds of Mn with P have been described Mn₃P an amorphous powder, SG 494, ob tained by heating Mn and P together to low red ness (Schrötter, J pr 51, 385) Also formed, according to H Rose, by heating MnCl₂ in PH₃ By heating Mn pyrophosphate mixed with sugarcharcoal, in a crucible filled up with charcoal, Struve (J pr 81, 321) obtained a brittle substance resembling pig iron, the composition of which varied between Mn₂P₂ and Mn₂P Merkel Merkel and Wohler (A 86, 371) obtained a crystalline, greyish, regulus, S G 5 95, by heating together 10 parts MnO, 10 parts well burnt bones, 5 parts quartz sand, and 3 parts lamp black The composition agreed with the formula Mn₅P₂, but as part was soluble, and part insoluble, in HClAq, they regarded the substance as a mixture of two phosphides, Mn₃P₂ (soluble in HClAq) and Mn₇P₂ (insoluble in HClAq)

Manganese, salts of Compounds obtained by replacing the H of acids by Mn Mn forms two series of salts manganous salts, MnX2, and manganic salts, Mn_2X_3 , $X = NO_3$, ClO_3 , $\frac{1}{2}SO_4$, $\frac{1}{2}PO_4$, &c One or two salts of the form $MnX_4 = g - Mn(SO_4)_2$ —are also said to exist. The manganous salts are considerably more stable than the manganic salts A number of double salts of manganic sulphate are known, those with the alkali sulphates are alums, eg Mn₂(SO₄)₃ K₂SO₄ 24H₂O The manganous salts form a fair number of double salts and a few basic salts The chief salts of Mn are the following antimonates, arsenates and arsenite, borate, carbonates, chlorate and perchlorate, chromates, ferri- and ferro cyanides, vodate, molybdate, nitrates and nitrites, phosphates and phosphites, selenates and selenites, silicates, sul phates and sulphites, throsulphate, tungstate, vanadate v Carbonates, Nitrates, Sulphates, &c

Manganese, selenide of Said to be produced in combination with H2O as a red powder, decomposed in air, by adding an alkali selenide so-

lution to solution of a manganous salt

Manganese, silicides of Mn and Si combine when heated together (Troost a Hautefeuille, C R 81, 264) Silicides of Mn, containing from 65 to 13 pc Si, have been obtained by Wohler (4 106, 54) by fusing together MnF., Na, K silicate, and cryolite, or MnCl. 2NaCl. CaF., and K silicate, or MnCl., CaF., K2SiF., and Na These silicates form hard, brittle masses, they dissolve in HClAq with evolution of H and SiH,

Manganese, silicofluoride of. MnSiF₆ 6H₂O Hexagonal crystals, ac=1 515, SG at 175°=19038 (Stolba, C C 1883 292) Formed by dissolving MnCO₃ or MnF₂ in H₂SiF₆Aq, and evaporating When heated, the crystals give off water, and then SiF4, and leave MnF2 (Berzelius)

Manganese, sulphides of Two sulphides are

known, MnS and MnS₂

MANGANOUS SULPHIDE, MnS Occurs native, as manganese blende, in hexagonal crystals, S G Produced by heating together MnO or MnCO, and S, not by heating S with Mr formed by heating Mn in CS2 (Gautier a Hallopeau, C R 108, 806), also by heating various Mn compounds in H_2S (Carnot, Bl [2] 32, 162) Sidot (J 1868 229) obtained MnS in hexagonal crystals by heating the amorphous substance in a stream of H_aS MnS is ppd from solutions of

Mn salts by NH, sulphide, as a pale buff coloured amorphous solid, which quickly oxidises in air, if this pp is rapidly dried and then warmed in H₂S, pure MnS is obtained MnS is a greenish solid, decomposed by weak soids, e g acetic soid, with evolution of H₂S. Heated in air, SO₂ is evolved and Mu₃O₄ remains (P. W. Hofmann, D. P. J. 181, 364). Heated in H₂O vapour, H₂S. and H are given off and Mn.O. is formed MnS is slowly decomposed by Cl with formation of MnCl, and S2Cl2

There appear to be two forms of MnS ob tainable by ppn from Mn salts by NH, sulphide the pp from conc MnCl₂Aq or MnSO₄Aq is rose coloured, if NH₄Cl is present the pp is greenish and consists of small 8 sided plates The green sulphide is not produced when K2S or Na,S is used as potant (Fresenius, J pr 82, 265, Muck, Z 1869 580, de Clermont a Guyot, Bl 27, 353, Geuther, Z 1865 347) The rose coloured sul phide is said to be changed to the green sulphide by heating with a little water, but it may be heated to 305° with much water without changing The change from rose to green is accomplished by heating with NH₃Aq to 250° in a closed tube, and the reverse change by heating in NH3 gas The rose sulphide is not changed by heating alone to 250° but in presence of H S the green sulphide is formed at 220° (De C a G, lc) The green sulphide is thought by Muck to be an oxysulphide of Mn

Double compound, 3MnS K2S Obtained by heating a mixture of 1 pt dry MnSO₄, ½ pt lamp-black, and 3 pts K2CO3 and S, and treat ing the fused mass with water, the compound remains insoluble in water, forming small lustrous

dark red tablets (Voelcker)

MANGANIC SULPHIDE, MnS. Occurs native as hauerte, in large, brown black, lustrous, regular octahedra, S G 3 463 Said to be obtained as a red amorphous powder, by heating MnSO₄Aq with solution of K polysulphides to 160°-180° in a closed tube (Senarmont, J pr 51, 385) Not changed in air, decomposed by acids

Manganese, sulphocyanide of, v vol n p
M M P M

MANGANITES Salts in which MnO2 acts as the acidic radicle, v Manganese peroxide, Reactions 12, under Manganese, Oxides and hydrated oxides of, p 183
MANGANOCYANIDES v vol 11 p 342

MANGOSTIN C₂₀H₂₂O₅ [c 190°] Contained in the husk of the fruit of Garcinia mangostana The dry husks are boiled with water to extract tannin, then treated with hot alcohol, and the alcoholic extract left to evaporate The man alcoholic extract left to evaporate gostin which is deposited is dissolved in alcohol and ppd by lead subacetate The pp is decomposed by water and the mangostin finally crys tallised from dilute alcohol (Schmid, A 93, 83) Thin golden lamine without taste or smell Insol water, v sol alcohol and ether Warm dilute acids dissolve it without alteration Hot conc HNO₃ gives oxalic acid Alkalis dissolve it with yellowish brown colour Reduces chloride FeCl, gives a dark greenish of gold solution black solution, decolourised by acids Its solution is not ppd by any metallic salt except lead sub acetate -(C20H21O3),5PbO (dried at 100°), ppd. by adding alcoholic lead acetate and ammonia to an alcoholic solution of mangostin

MANNITE C.H., O, te CH., (OH) CH(OH) CH(OH) CH(OH) CH, (OH) Mol w 182 (181 by Raoult's method, Brown a. Morris, C J 58, 620) [165°] S G 15 [α]_D = -25 8 156 at 18° (Berthelot, A Ch [3] 47, 301), 13 at 14° (Krusemann, B 9, 1467), 16 at 16 5° (Wanklyn a Erlenmeyer, J 1862 480) S (alcohol) 07 at 14° H C v 728,200 H C p 728,500 (Berthelot a Vieille, Bl [2] 47, 868, A Ch [6] 10, 456) HF 318,500 (B a V), 287,000 (Von Rechenberg)

Occurrence -Discovered by Proust (A Ch [1] 57, 143) Occurs to the extent of 30 to 60 pc in manna, the aried juice which exudes from the manna ash (Frazinus Ornus) Mannite occurs in many other plants, eg the roots of Aconitum napellus, celery, Apium graveolens, Meum athamanticum, Enanthe crocata, Poly podium vulgare, Scorzonera hispanica, and Triticum repens, and in the root bank of Tunica granatum Mannite also occurs in the bark of Canella alba (8 pc), and of Fraxinus excelsior, in the leaves and voung twigs of Syringa vulgaris, in the leaves of Liquis trum vulgare and of Cocos nucifera, and in the fruit of Laurus Persea and of Cactus opuntia Mannite also occurs in Laminaria saccharina, in olives, and in several fungi, eg Lactarius rellereus, L turpis, L pyrogalus, and L palli dus Aganeus integer contains 20 p c of its dry substance It also occurs in the cambium layer of Conifera (Payen, A 12, 60, Meyer a Reiche, A 47, 234, Stenhouse, A 51, 349, Knop a Schnedermann, A 49, 293, Dopping a Schloss beiger, A 52, 117, Muntz, CR 76, 649, 82, 210, Smith J 1850, 545, Roussin, J 1851, 550, Ludwig, J 1857, 503, De Luca, J 1861, 740, 1862, 505, Thorner, B 12, 1635, Reinsch, J 1863, 612, Bourquelot, C R 108, 568, Kuchler, M 7, 410)

Formation -1 In the lactic fermentation of sugar (Liebig, J 1847, 466, Pasteur, J 1857, 511, Diagendorff, Ar Ph [3] 15, 47) -2 In the vi-cous fermentation of sugar, 100 pts of sugar yielding 51 pts mannite and 46 pts gum (Pis teur, J 1861, 728) – 3 In the spontaneous fer mentation of the juice of the sugar cane in tropical climates (Maicano, C h 108, 955) -4 by reducing glucose, lavulose, or invert sugar with sodium amalgam (Linnemann, A 123 136, Dewar, P M [4] 39, 345, Bouchaidat, Bl [2] 16, 38, Krusemann B 9, 1465, Scheibler, B 16, 3010) -5 By reducing mannose (Γ Fischer, B 21, 1808), or 'glucosone' (L Fischer, B 22, 94), with sodium amalgam -6 From the dilac tone of meta sacchanic acid by treating with weter and sodium amalgam (3 p c), acidifying with H₂SO₄ (Kiliani, B 20, 2714, v L ±vo-MANNITE, infia)

Preparation -1 Manna is extracted with boiling dilute alcohol, and the crystals which separate on cooling are recrystallised from water -2 Manna (2 pts) is boiled with water (1 pt) after addition of a little white of egg The crystals which separate from the filtrate are boiled with water (6 pts) to which some animal charcoal has been added, and the filtrate is allowed to crystallise (Ruspini, A 65, 203)

Properties - Needles or four sided prisms V sol water, v al sol alcohol, insol ether An aqueous solution, does not become syrupy on

spontaneous evaporation (difference from sugar) Only slightly sweet to the taste It has little, if any, action on light, but if borax be added to the solution it becomes dextrorotatory in a 10 pc solution containing 12 8 g borax $\alpha = +22.5^{\circ}$, so that $[\alpha]_{\rm p} = c + 225^{\circ}$ (Vignon, A Ch [5] 2,433, C R 77, 1191, Muntz a Aubin, C R 83, 1213, Pasteur, C R 77, 1192, Bouchardat, C R 80, 120, 84, 34) Arsenic acid slowly develops levorotation in a solution of mannite Salts of the alkalis and alkaline earths develop dextrorotation Free alkalis render the solution lævoiotatory A solution containing 8 g mannite and 8 g NaOH in 100 cc gives $a = -34^{\circ}$, so that $[a]_{D} = -42^{\circ}$ A solution of 12 g mannite and 4 g sodium tungstate made up to 100 cc shows $a = +0^{\circ} 40'$ (Klein, C R 89, 484) These rotations vary with the amount of dissolved substances The mannite may be recovered from these solutions without having undergone any change in optical properties Mannite renders a borax solution acid, forming boracic acid and sodium metaborate (Dunstan, Ph [3] 13, 257, 14, 41, Lambert, \hat{C} R 108, 1016) Mannite does not reduce Fehling s solu It hinders the ppn of ferric and cupric salts by potash It is not turned brown by boil ıng KÖHAq With a solution of ammonio sulphate of copper it gives a blue pp, sol in ammonia, forming a blue solution which is not affected by boiling (Guignet, C R 109, 528, 645) Mannite does not reduce boiling solutions of silver or mercurous nitiates, of HgCl, or of chloride of gold, but it reduces Ag O and silver acetate (Hirzel, A 131, 50) When alcohol is added to a solution of mannite mixed with lime, strontia, or baiyta water, pps (C₆H₁₄O₆)₄3CaO, (C₆H₁₄O₆)₄SrO, and (C₆H₁₄O₆)₂BaO are formed (Hirzel, A 131, 50, of Ubaldini, A Ch [3] 57, 213) Ammoniacal lead acetate gives a pp On adding to an aqueous solution of mannite (1 mol) and of lead nitrate (2 mols) sufficient ammonia to neutralise two thirds of the nitric acid present in the salt, a voluminous white pp separates, which, if fitered off and dried over calcium chloride, forms a white crystalline powder C₈H₈O₅Pb₄(NO₃)₂2H₂O, S 1 10 at 14°, decom posing with explosion on heating, and separated into its constituents on long boiling with water and by carbonic anhydride with formation of lead carbonate (Smolka, M 6, 198)

Reactions -1 Mannite begins to sublime at

c 200, in a sealed tube it is unaltered at 250° At 280° it splits up into water and mannitan C.H.O. When distilled in vacuo it yields isomannia. C.H.O. —2 A mixture of HNO, and H.SO, forms the nitrate, so called 'nitro mannite ' (Flores Domonte a Menard, J 1847. 1145) -3 Nitric acid oxidises it to saccharic, racemic, and oxalic acids, no mucic acid being formed (Backhaus, J 1860, 522, Carlet, J 1861, 367) -4 Boiling HIAq gives sec-hexyl iodide (Wanklyn a Erlenmeyer, Domac, M 2, 309, cf Le Bel a Wassermann, C R 100, 1589) -5 Boiling cone HClAq slowly forms mannitan — 6 Potash fusion yields formic, acetic, and propionic and oxalic acids and acetone (Gottlieb, A 52, 122) -7 On oxidation with KMnO in alkaline solution it gives oxalic acid, formic acid, a little tartaric acid, a sugar which reduces Fehling's solution, and erythric acid C,H,O,, which forms 190 MANNITE.

the salts CaA'₂ 2aq, BaA'₂ 2aq, and C₄H₆BaO₅ 2aq (Hecht a Iwig, B 14, 1760, 19, 468, cf Pabst, C. R 91, 728, who states that he obtained a dibasic acid $C_0H_0O_0$, which he names dioxyisocitric acid) —8 Air and $platinum\ black\ yield\ mannitio acid <math>C_0H_{12}O_0$, and mannitose $C_0H_{12}O_0$. 9 MnO₂ and H₂SO₄ give formic acid and acrolein (Backhaus) —10 When mannite (2 pts) is heated with 80 pc formic acid (5 pts) for 8 hours a mixture of formyl derivatives of mannitan appears to be formed This mixture yields on distillation CO, CO₂, isomannide C₅H₁₀O₄, a liquid C₆H₁₆O₅ (?) (157° at 17 mm) and a liquid C₆H₈O (108°), S G $\frac{9}{4}$ 9396, $[a]_{\rm p} = -168°$, almost insol water, and smelling like a carbamine and mustard oil (Fauconnier, C R 100, 914, cf Henninger, B 7, 264) -11 Distillation with oxalic acid yields formic acid, a formyl derivative of mannite or of mannitan being probably first formed (Lorin, Bl~[2]24,437)—12 Electrolysis of a solution of mannite acidulated by H_2SO_4 yields hydrogen, CO2, CO, oxygen, tri oxy methylene (? formic paraldehyde or mannitose), formic acid, oxalic acid, and a small quantity of an acid whose calcium salt is C₆H₆CaO₈ 2aq This acid having

reducing properties may be CO'H CO (CH OH)2 CO'H (Rénard, A Ch [5] 17, 316) -13 PCl, gives tetra chloro-hexmane (Bell, B 12,1273) —14 PI, forms methylene iodide (Butlerow, A 111,247) — 15 Organic acids (e.g. acetic and butyric) heated with mannite at 200° form alkoyl derivatives of mannitan - 16 Mannite heated with uater suffers no change below 280°, but at that tem perature a viscid product is got containing 'mannitic ether ' $C_{12}H_{28}O_{11}$ ([a]_j = -56) and 'mannitone,' a crystalline isomeride of mannitan Both bodies are reconverted into mannite by heating with water at 295° (Vignon).—17 Mannite does not react when heated with acetic, valeric, or benzoic aldehydes (Lochert, A Ch [6] 16, 65) But when acetic aldehyde is passed into a solution of mannite in H₂SO₄ or HClAq the alde hyde is absorbed and there is formed a compound crystallising in needles [174°], insol cold water S 1 at 95° It is sl sol cold, v sol hot, alcohol Boiling dilute (2 pc) H_2SO_4 resolves it into aldehyde and mannite Paraldehyde gives the same compound When a mixture of acetic and benzoic aldehydes is used the above product is formed first (Meunier, C R 108, 408) -18 When a mixture of mannite (10 g), absolute alcohol (20 g), and fused ZnCl₂ (5 g) is saturated with HCl, left for two days, and then mixed with benzoic aldehyde, there is formed 'tribenzoic mannitoid' $C_cH_sO_s(C,H_cO)_s$ [207°] This crystal lises from benzene, and is insol water, sl sol alcohol It is not affected by boiling alcoholic KOH, but dilute H2SO4 yields mannite and benzoic aldehyde (Meunier, C R 106, 1425, A solution of mannite in HClAq or H.SO. also reacts with benzoic aldehyde (Meunier, CR 107, 910) -19 A solution of mannite in alcohol containing ZnCl₂ and saturated with HCl reacts with BzCl, forming di-benzoyl mannide C.H.O.(OBz), [132°] (Meunier, C R 107, 346) 20 Valeric aldehyde, ZnCl, and HCl convert mannate in alcoholic solution into C₆H₄O₅(C₅H₁₆O)₅, which is deposited as silky needles [91°] (Meunier) -21 Not fermented by yeast In contact with water, chalk, and cheese at 40° it gives

alcohol, carbonic, lactic, butyric, and acetic acids. and hydrogen, but no sugar or glycerin (Berthelot, J 1856, 664) When the fermentation is induced by a slit testicle a fermentible sugar is produced Upon fermentation by Schizomycetes in presence of CaCO, and ammonium phosphate there is formed alcohol, n butyl alcohol, butyric, lactic, acetic, hexoic, and succinic acids (Fitz, B 10, 281, 11, 43) Bacillus butyricus gives similar products Under other conditions formic acid is among the products of fermentation (Fitz, B 11,

among the products of fermentation [Fitz, B 11, 1895, 15, 876, 16, 845) —22 Heating with phenyl cyanate forms $C_nH_0(OH)(OCONHPh)$, [260°] (Tessmer, B 18, 96s)

Pentanitrate $C_nH_0(ONO)$, O Pentanitroxyl derivative [79°] S 2 at 60° S (alcohol, S G ?1) 150 at 12 8° S (ether) 180 at 9° Formed, together with nitro mannitan, by pass ing NH₃ into an ethereal solution of the hexa nitrate (Tichanovitch, J 1864, 582) Long needles Dextrorotatory Explodes when struck, and also, more feebly, when heated Ammonium

sulphide reduces it to mannite

Hexanitrate C,H₈(ONO),O Nitro mannite Mol w 452 [113°] (Socoloff) S G 2 1604 S (alcohol of S G 81) 3 at 128° S (ether) 5 at 9° (Tichanovitch) $\alpha = +12.4$ in a 3 p c solution, so that $[a]_D = +400^\circ$ (Muntz a Aubin) Piepared by treating mannite (1 pt) with HNO₃ (5 pts of S G 1 5) at 0°, and adding H₂SO₄ (10 pts) The product is collected on a filter, washed with water and aqueous Na CO3, and recrystallised from alcohol (Domont a Menard, J 1847, 1145, Sobrero, A 64, 397, Strecker, A 73, 62, Socoloff, J R 11, 136) Beautiful white needles, insol water, sol alcohol and ether Explodes violently on being struckit also explodes when suddenly heated, but if carefully heated it may be decomposed without explosion Ammonium sulphide conveits it into mannite (Dessaignes, A 81, 251) Inon and acetic acid and HIAq also convert it into man nite (Bechamp, A Ch [3] 46, 354, Mills, J 1864, 584) NH, passed into its ethereal solu tion forms crystalline C.H.O(NH.), (Tichano

Disulphuric acid CoH8(SO4H)2(OH)4. From mannite and conc H2SO4 (Favie, B J 25, 560) The free acid is decomposed by boil-

ing water It gives no pp with BaCl₂ or CaCl₂ —
Pb₂C₆H₁₀S O₁₂2PbO insoluble pp
Tri sulphuric acid C₆H₁₀(SO₄H)₄(OH)₄ From mannite and conc H.SO, (knop a Schnedermann, A 51, 130) Both the acid and its salts are decomposed by water into mannite and H₂SO₄—Na₃A"—K₃A" deliquescent gummy mass, insol alcohol—Ba₃A"₂ crystal line powder, sol water, insol alcohol—Pb₃A'₂ amorphous deliquescent mass

Tetra sulphuric acid $C_0H_2(SO_4H)_4(OH)_2$ [a]_D = +9° Obtained when, in the preparation of the hexa sulphuric acid, the neutralisation with BaCO, is delayed for two

days --- Ba2Aiv

Hexa-sulphur c acid $C_eH_s(SO_4H)_e$.

[a]_D = +24° Formed by adding mannite in small portions to chloro sulphuric acid (CISO.H) The product is dropped upon ice, and the ice solution neutralised with BaCO,cold Ba, Avi 5aq When alcohol is added to its solution this salt is thrown down as an oil, which presently changes to a crystalline mass insol The other salts are very soluble, and do not behave thus (Claesson, J pr [2] 20, 10)

Boric acid When mannite (4 pts) is heated with boric acid (3 pts) for eight hours at 145°, and the product is dissolved in water and neutralised by BaCO₃, a filtrate is obtained which deposits barium borate on evaporating, after which alcohol gives a pp which, when dried at 100°, has the composition (C₆H₁₃B₂O₆) Ba (Klein, Bl [2] 29, 363)

Hexa acetyl derivative C.H. (OAc), [119°] [α]_D = +18° (Bouchardat, C R 84, 34) From mannite (18 pts) and Ac₂O (80 pts) at 180°, with or without addition of a little ZnCl, (Bouchardat, A Ch [5] 6, 107, Schutzenberger, A 160, 94, Franchimont, B 12 2059) Limit of etherication from mannite (1 mol) and HOAc (6 mols) 264 (Menschutkin, B 13, Trimetric crystals (from HOAc) Insol water, cold alcohol, and ether, sl sol hot alco Destrorotatory hol May be sublimed in a current of CO

Penta benzoyl derivative

 $C_{e}H_{o}(OBz)_{s}(OH)$ [c 80°] From mannite (3 g), water (15 g), BzCl (20 g), and NaOHAq product is extracted with ether (Skraup, M 10, 391) Amorphous mass

Hera benzoyl derivative CH,(OBz), [149° From the preceding and BzCl Crystal

line grains, v sl sol alcohol

Mannite dichlorhydrin $C_1H_8(OH)_1Cl_2$ Dichloro tetra oxy herani [174°] S 4 5 at 14° [a]_D = -37 Formed by heating mannite (1 pt) with cone HClAq (6 pts) at 100° for eight hours (Bouch adat, C R 75, 1187, 76 1550, Bl [2] 19, 199) Formed also by heating isomannide with furning HClAq at 100° in sealed tubes (Fauconniei, Bl [2] 41, 119) Prepared by heating mannite (1 pt) with fuming HClAq (10 pts) at 106°, evaporating at low temperatures. dissolving the crystals in water filtering the solution through animal charcoal, and re crystallising from hot alcohol (Siwoloboff, A 233, 368)

Properties - Monoclinic crystals Lavoro tatory Its aqueous solution is neutral and tasteless, and is not ppd by AgNO, Insol alcohol and ether Decomposed on fusion

Reactions -1 Boiling water or conc NaOHAq rapidly convert it into C_eH₈O(OH)₃Cl -2 A of HNO and H,SO, C,H,(ONO2)4Cl2, which crystallises from hot alcohol in needles [145°], insol water —3 So dium amalgam removes HCl in two stages, forming mannitan chlorhydrin, and finally (3) mannide [119°]

Mannite dibromhydrin C_eH_s(OH), Br [178°] Obtained by heating mannite with conc HBrAq for 2 hours at 100° (Bouchardat, A Ch [5] 6, 120) Small colourless plates (from hot water) Decomposed on fusion Insol cold water, al cohol, and ether Converted by a mixture of HNO, and H₂SO₄ into C₂H₃(ONO₂)₄Br₂, which crystallises in long needlas, sol hot alcohol, msol water

Mannitan C₆H₁₂O₅ is C₆H₈O(OH)₄ anhydride of mannite According to Alechin (J R 16, 883) the various mannitans described below are mixtures of isomannide and other bodies

(a) Berthelot's mannitan CeH12O3 Obtained in small quantity by heating mannite at 200° A better method is by protracted boiling of man nite with cone HClAq (Berthelot, A Ch [3] 47, 306) Slightly sweetish syrup Differs from mannite in being soluble in absolute alcohol-V sol water, insol ether Slightly de tatory (Bouchardat, A Ch [5] 6, 102) Slightly dextroroexposed to the atmosphere it is partially reconverted into mannite Boiling alkalis or dilute acids accelerate the change Above 140° it partly volatilises

(b) Vignon's mannitan C_6H_1 , O_5 [a]_j = +36 5° Prepared by heating mannite for an hour or two with half its weight of water at 295° Also by heating mannite (2 pts) with conc H SO, (1 pt) at 120°, saturating with BaCO, exhausting with alcohol, and evaporating (Vignon, A Ch [5] 2, 433) Deliquescent mass, v e sol water and absolute alcohol, insol ether Does not ferment with yeast Boiling dilute H.SO, or baryta water does not reconvert it into mannite Amix ture of mannitan (1 pt), $H_{\circ}SO_{+}$ (10 pts), and HNO_{3} (41 pts of SG 15) forms in the cold C, H, O (OH)(ONO), which is obtained on pouring into water and extracting with ether. It is dex trorotatory $[a]_i = +53^\circ$

(c) Vianon's mannitone $C_0H_1O_2$ [a] = -25° Obtained by heating mannite with water for 3 hours at 280° and extracting the viscid product with alcohol (Vignon, A Ch [5] 2, 433) Has a sweet taste Lævo tals (from alcohol) rotatory Does not reduce Fehling's solution In the preparation of this body the syrupy mother liquor yields a viscid mass, which appears to be the anhydride of mannite or 'mannitic ether 'C, H.,O,, it does not reduce Fehling's solution, and is levolotatory, $[a]_j = -5.6^{\circ}$ This mannitic ether is not converted into mannite or munnitan by boiling dilute acids or alkalis

(d) Crystalline mannitan C.H. O. S 25 at When Berthelot's mannitan is allowed to stand for some months in a dry atmosphere it deposits a solid variety (Bouchardat) This crystallises in monoclinic tables It is strongly hevorotatory Sl sol cold alcohol Boiling water quickly converts it into mannite variety of mannitan is probably identical with Vignon's

Mannetan tetra netrate C, H,O(ONO). Precipitated by adding water to the alcoholis mother liquor from which mannite pentanitrate has separated (Tichanovitch, J 1864, 583) Syrup, v sol alcohol and ether, insol water Explodes when struck Alcoholic KOH converts it slowly into_syrupy mannitan

Di acetyl derivative C.H.O(OH)2(OAc). From mannite and HOAc at 210 $\lceil \alpha \rceil = +226$ Mannite dissolves in boiling Ac2O, (Berthelot) and on cooling crystals of C1 H2AcO10 separate Further action of Ac O yields hexa acetyl man nite and di acetyl mannitan (Schutzenberger, A 160, 74, Grange, C R 68, 1326) Extremely bitter substance, v sol water, HOAc, and alcohol Dextrorotatory Boiling baryta water converts it into acetic acid and mannitan

Tetra acetyl derivative C.H.O(OAc), Formed, together with hexa acetyl mannite, by heating mannite with Ac,O at 180° (Bouchardat, A Ch [5] 6, 110) Amorphous viscid mass, which partially crystallises on long standing

192 MANNITE.

Insol water, v e. sol alcohol, ether, and HOAc Dextrorotatory Aqueous alkalıs at 100° decompose it into acetic acid and mannitan Ac.O forms hexa-acetyl mannite A mixture of HNO. and H2SO4 has no action in the cold

Ds-butyry l derivative

C₅H₂O(O(H₂O)₂(OH)₂ From mannite and butyric acid at 200° (Berthelot, C R 38, 673, A Ch [3] 47, 319) Semi solid, partly crystalline, mass Insol water, v sol alcohol and ether

Tetra butyryl derivative

 $C_{\rm e}H_{\rm e}O({\rm OC}_4H_7{\rm O})_4$ From mannite and excess of butyric acid at 200°-250° Oil

Di-benzoyl derivative

C₆H₈O(OBz)₂(OH)₂ From mannite and HOBz at 200° (Berthelot, Chimie organique, 2, 193) Soft resin, v e sol alcohol and ether

Di-ethyl derivative C₆H₈O(OH)₂(OEt)₂ From mannite, KOH, and EtBr at 100° (Berthelot) Syrup, v sl sol water, sol alcohol, v e

sol ether

Mannitan chlorhydrin C,H,O(OH),Cl From mannite dichlorhydrin by boiling for two hours with 100 pts of water, neutralising with K₂CO₃, evaporating, and extracting with ether (Bouchardat, A Ch [5] 6, 118) Solid mass, v e sol water, alcohol, and ether Dextrorotatory Conc HClAq at 100° reconverts it into mannite dichlorhydrin Boiling water converts it into HCl and mannitan

Mannitan dichlorhydrin From mannite (1 pt) and $\mathbf{C_6H_8O(OH)_2Cl_2}$ fuming HClAq (15 pts) by heating for 3 days at 100° (Berthelot, J 1856, 661) Crystals, sol ether KOHAq converts it into mannitan

Mannitan bromhydrin C,H,O(OH),Br From mannite dibromhydrin by boiling with water V e sol water, alcohol, and ether Dextrorotatory

Mannide C.H.O. Second anhydride of

mannite

(a) Berthelot's mannide C₆H₁₀O₄ (297°-317°) Obtained by heating mannite with butyric acid at 200° - 250° (Berthelot, A Ch [3] 47, 312, Liebermann, B 17, 874) Thick deliquescent syrup, v e sol cold water and alcohol Decomposes partially on distillation In contact with

the air it partially forms mannite

(b) (β)-Mannide C₆H₁₆O₄ [119°] (212° at 16 mm) S 150 at 15° S (alcohol) 2 7 at -16°, 78 at 12° Obtained by treating mannite dichlorhydrin with sodium amalgam (Siwoloboff, A 233, 368) Prisms, v e sol water and alcohol, insol ether Dextrorotatory Sublimes at 14°, forming long needles Does not yield mannite when heated with water Air and platinum black oxidise it, forming a syrupy liquid

(c) Isomannide C₆H₁₀O₄ i e 0

СН₂(ОН) СН СН СН СН СН ОН ? [87°] (176° at 30 mm) $(274^{\circ} \text{ at } 760 \text{ mm})$ $[a]_{D} = +914 \text{ m}$ a 6 p c aqueous solution Obtained by distilling mannite in vacuo, the product being fractionally distilled in vacuo (Fauconnier, C R 95, 991) Prepared by boiling mannite (200 g) with HClAq (2,000 g) for 24 hours, cooling, filtering, and distilling in vacuo The distillate is allowed to stand for a fortnight, extracted with cold alcohol, the extract distilled in vacuo, and the frac-

tion boiling at 176° recrystallised from alcohol (Fauconnier, Bl [2] 41, 119) Large monoclinic, somewhat deliquescent, crystals Boils at 2740 with partial decomposition V e sol water, m sol alcohol, sl sol chloroform, msol ether and benzene Dextrorotatory Not affected by heating with water at 150° By heating with fuming HClAq in sealed tubes at 100° for 25 days it is converted into mannite dichlorhydrin $C_dH_s(OH)_4Cl_2$ [174°] It is not acted upon by POCls, by bromine in the cold, or by sodiumamalgam

Di-formyl derivat ve C.H.O. (OCHO)2. [115°] (166° at 18 mm) Small plates, sl. sol

cold water, v sol alcohol, sol ether

Acetyl derivative C₆H₈O₂(OH)(OAc) (186° at 25 mm.) From isomannide and Ac₂O Colourless oil, sol ether

Dr-acety'l derivative $C_{\mathfrak{g}}H_{\mathfrak{g}}O_{\mathfrak{g}}(OAc)$ (198° at 28 mm) From isomannide (1 pt) by boiling with Ac.O (3 pts) for 8 hours Viscid boiling with Ac₂O (3 pts) for 8 hours Viscid liquid, with bitter taste Not altered by further treatment with Ac2O

Di-benzoyl derivative C,H,O,(OBz), [132°] From mannite, alcohol, ZnČl₂, HČl, and BzCl (Meunier, C R 107, 346) Monoclinic or triclinic ciystals, v sl sol water and cold alco hol, sol chloroform and benzene Not decom posed by queous acids or alkalis

Methyl derivative C₆H₈O₂(OH)(OMe) [48°] (174° at 24 mm) From isomannide, KOH, MeI, and a little water at 150° Crystals

Ethyl derivative C₆H₆O₂(OH)(OEt) (165° at 17 mm) Formed by heating mannite, $C_aH_aO_2(OH)(OEt)$ EtI, and conc KOHAq in sealed tubes for 4 hours at 120° Colourless mobile liquid, sol water, alcohol, and ether

Isomannide dichlorhydrin C, H,O2Cl2 [49°] (143° at 43 mm) From isomannide (1 pt) by warming with PCl_s (2 pts) White needles or plates, v sol ether, m sol alcohol insol cold, sol hot, water Has a strong aro matic odour and a peppery taste May be dis tilled with steam It is very stable, not being attacked by alcoholic KOH at 150°, by PCl, at 125°, or by sodium amalgam

Anhydride of mannide $C_{12}H_{18}O_7$ is (C₆H₈O₂OH),O (?) Deposited on standing from a sample of butyric acid (Geuther, A 221, 59)

Levo mannite C₆H₁₄O₅ [164°] Formed by reducing levo mannose with sodium amalgam. Globular groups of fine needles, v sol water, sl sol absolute alcohol, much more sol methyl alcohol It tastes sweet, and does not reduce Fehling's solution A solution of this mannite containing borax turns the ray of polarised light to the left This substance is probably the one obtained by Kiliani (B 20, 2714) by reduction of the double lactone of metasaccharic acid (Emil Fischer, B 23, 375)

Inactive mannite a Acrite [168°] Formed by reducing inactive mannose with sodiumamalgam Small prisms (from water), v sol water, m sol hot giacial acetic acid, sl sol methyl and ethyl alcohols It is easily distin guished from ordinary mannite by its crystalline form and by its optical mactivity A solution containing borax remains wholly inactive This mannite is identical with (a) acrite, a substance obtained by the action of sodium amalgam on (a)-acrose, a sugar obtained by the action of alkalıs on acrolein dibromide (Fischer, B 22, 100) By oxidation with dilute HNO, mactive mannose is formed (Emil Fischer, B 23, 383)

The mannites may be distinguished optically by means of their phenyl hydrazides 1 g of the phenyl hydrazide dissolved in 1 c c of cold conc HClAq and 5 c c of water gives in a tube 100 mm long a rotation of $+12^{\circ}$, -12° , and 0° , with the lævo-, dextro , and mactive mannite respectively In the course of 3 or 4 hours the rotation vanishes, the phenyl hydrazide being decomposed by the HCl When the di phenyl dihydrazide is used 1 g is dissolved in warm HOAc, cooled, and examined in a 100 mm tube gives a rotation of $+0.85^{\circ}$, -0.85° , or 0° in the case of the lævo, dextro, and mactive compounds respectively The dextro and lævo mannites themselves scarcely exhibit a rotation, but 15g of the mannite dissolved in 5 cc water containing $37 \, \mathrm{g}$ borax exhibits a rotation of $+0.85^{\circ}$, -0.85° , or 0° , according as the mannite 18 dextro, lævo, or mactive (Fischer)

MANNITIC ACID C.H.2O, Prepared by mixing mannite (2 g) with platinum black (4 g), moistened with water, and exposing the mixture at 30° to 40° to the air for 3 weeks The mass is then exhausted with water, the solution ppd. by lead subacetate, the pp decomposed by H2S, and the solution evaporated in the cold over H₂SO₄ (Gorup Besanez, A 118, 257) Gummy mass, sol water and alcohol, nearly insolether. It is a strong acid, and dissolves zince with evolution of hydrogen. It begins to de compose at 80°. It reduces silver nitrate solution and hot Fehling's solution It is ppd by baryta and by lime water —CaA" amorphous powder, ppd by adding alcohol to its aqueous solution CuA" green amorphous mass left by evaporating its solution -PbA" granular Ag.A" curdy pp

MANNITINE C₆H₈N₂ (170°) Prepared by distilling a mixture of mannite (1 mol) and ammonium chloride (2 mols) The distillate is mixed with KOHAq and shaken with ether (Scichilone a Denaro, G 12, 416, Etard, C R 92, 795) Brown oil, with strong odour, sol alcohol and ether, m sol water Gives an orange yellow pp with sodium phosphomolybdate, a reddish yellow pp with iodine in KIAq, a pink pp with HgCl, and a black pp with aurio chloride Hypodermically injected it produces diminution of the cardiac systole, and irregular respiration, followed by insensibility and death

MANNITOSE C.H.₁₂O₄ Produced, together with mannitic acid, by the atmospheric oxidation of mannite in the presence of platinum black (Gorup Besanez, A 118, 273) Optically Fermentable Reacts like glucose with alkalis, Fehling's solution, basic bismuth nitrate, and Na_2CO_3 , but it does not unite with NaCl Its alcoholic solution gives with alcoholic potash a pp of $(C_3H_{12}O_3)_2K_2O$ Mannitose is perhaps identical with levilose (Dafert, B 17, **228** , **19**, 911)

MANNONIC ACIDS C.H.2O,

Inactive mannonic acid Lactona C.H., O. [155°] Formed from inactive mannose by oxidation with bromine (E Fischer, B. 28, 876)
Long glittering prisms, grouped in stars or
Vol. III

needles (from alcohol), v sol hot water, sl sol hot alcohol Has a sweet taste and does not reduce Fehling's solution By means of the strychnine salt it can be split up into dextromannonic acid and arabinose carboxylic acid, the strychnine salt of the latter being extremely sl sol alcohol The morphine salts may also be employed, morphine dextro mannonate crystallising out Penicillium glaucum partly decom poses mactive mannonic acid, liberating some arabinose carboxylic acid -- Ca(C₈H₁₁O₇)₂ Groups of slender needles Less soluble than calcium ævo mannonate

Phenyl hydraside C₁₂H₁₈N₂O₆ [230°] Colourless cubes, sl sol hot water, v sl sol alcohol Solder had been solder by the solder Phenyl hydraside C12H16N2O6 cohol Split up by hot baryta water into phenyl hydrazine and inactive mannonic acid

Dextro-mannonic acid Formed from gluconic acid by heating with twice its weight of quinoline for 40 minutes to 140° (Emil Fischer, B 23, 801) Formed also as above and by oxidation of dextro mannose by bromine By heating dextro mannonic acid with quinoline, gluconic acid is formed For this purpose 20 g of dextro mannonic acid, 5g water, and 40g quinoline are heated to 140° for 40 minutes The unchanged mannonic acid is separated by means of its brucine salt Dextro mannonic acid, like the other mannonic acids, when liberated from its salts condenses at once to the lactone CaH10Oa [149°-153°] Its rotation, $[\alpha]_D = 53.8$, is equal and opposite to that of the lactone of arabinosecarboxylic acid, which is therefore levo mannonic acid

Salts -Ca(C₈H₁₁O₁) 2aq -Si A'₂3aq -BaA'₂

(dried at 100°)

Phenyl hydrazide C1H18N2O6 Small colourless prisms, v sol, hot water De composed by hot baryta water into dextro man nonic acid and phenyl hydrazine

Lactone C₆H₁₀O₆ icul [145°-150°] Lævo-mannonic acid carboxylicaculArabinose $[a]_{D} = -548$ Formed from anabinose (v Arabid ACID and SUGARS) by treatment with HCy and sa ponification of the product (Kiliani, B 19, 3033) Formed also from mactive mannonic acid, as above

MANNOSE C.H., O. 16
CHO CH(OH) CH(OH) CH(OH) CH(OH) CH(OH)

Dextro mannose [a]_D = +13° Formed by heat ing 3 kilos of mannite with 20 litres of water and 10 litres of HNO, (SG 141) in the water bath with shaking to 40°-45° until a test portion rendered neutral with soda gives a thick paleyellow pp of the hydrazide with phenyl-hydra The whole is then cooled with zine acetate ice to about 25°, made feebly alkaline with crystallised Na₂CO₃, acidified with acetic acid, and treated with 1 kilo of phenylhydrazine dissolved in dilute acetic acid. The phenylhydrazide crystallised from hot water is con verted into the sugar by solution in HCl (S G 1 19), allowing to stand, cooling, filtering, and neutralising the diluted filtrate with pure car-bonate of lead The whole is again filtered, made alkaline with Ba(OH), and shaken with ether The aqueous solution separated from ether contains the sugar, which remains as a syru, on evaporating, and is ppd from absolute alcohol by ether (Emil Fischer a, Josef Hirschberger, B 21, 1806, 22, 365), Mannos may more easily be got from vegetable ivory nuts, v SEMINOSE infra

Properties — Light yellow syrup, with sweet taste V sol water and alcohol Reduces Fehling's solution, 1 cc corresponding to 004307g of mannose Turned brown by heating with 20 p c HClAq, the solution then containing levulic acid Ferments easily with yeast, giving CO, and alcohol The aqueous solution is dex trorotatory, but less so than glucose Sodiumamalgam (2 p c) reduces mannose to mannite Furfuraldehyde is formed by heating a dilute solution of mannose at 110° for four hours

AcCl forms a substance like acetochlorhydrose Phenyl hydrazide C₁₂H₁₈N₂O₅ [195° 200°] S 1 at 100° Prepared as above Slender prisms (from water) Sl sol alcohol and acetone Its solution in dilute HClAq is levorotatory Concentrated mineral acids convert it into mannite and phenyl hydrazine even in the cold When it is heated with phenyl hydrazine hydrochloride (3 pts), NaOAc (4 pts) and water (80 pts) at 105° for 4 hours there is formed the 'osazone' of glucose C18H22N4O4, which crystallises from alcohol in slender yellow needles [206°]

Oxim C₆H₁₃O₆N Crystalline, ▼ sol hot water, insol alcohol When slowly heated it melts at 176°-180°, but when quickly heated, at 184° (Fischer a Hirschberger, B 22, 1155)

Inactive mannose Formed by reducing the lactone of mactive mannonic acid with sodiumamalgam (E Fischer, B 23, 381) Colourless syrup, v sol water, sl sol absolute alcohol, m sol hot methyl alcohol Resembles (dextro) mannose except in being inactive When subjected to fermentation levo mannose is left Bromine oxidises it to inactive mannonic acid

Phenyl hydrazide [195°] Decomposed on fusion Sl sol water Its solution in HCl is optically mactive Cold cone HCl splits it up

into sugar and phenyl hydrazine

Di-phenyl hydrazide C18H22N4O4 [218°] Formed by heating the mactive mannose with phenyl hydrazine (2 mols), the corresponding quantity of acetic acid and water Fine yellow glittering needles, sl sol water, cold alcohol, and ether Decomposes on fusion At 45° conc HCl forms the corresponding osone The solution in 60 pts glacial acetic acid is optically The properties of this diphenylhydrazide are the same as those of (a) acrosazone (the di phenyl hydrazide of (a) acrose), and Emil Fischer (B 23, 383) considers that they are identical

Lævo-mannose To prepare this body 1 pt of the lactone of arabinose carboxylic acid is dissolved in 10 pts water, acidified with H.SO., and cooled to 0° 2½ pc sodium amalgam is added in small portions The liquid must re main acid Colourless syrup, v sol water, sl sol absolute alcohol, m sol methyl alcohol The aqueous solution is slightly lævorotatory It ferments little, if at all, with yeast

Phenyl hydrazide C₁₂H₁₈N₂O₅ [195°] Formed by adding phenyl-hydrazine acetate to a solution of the sugar Slender, almost colour less crystals It is more sol water than the dextro mannose phenyl hydrazide The hydro chloric acid solution is dextrorotatory 'Cold HCl splits up the compound into phenyl-

hydrazine and mannose

Di-phenyl hydraside [2050] Formed by heating the lævo mannose phenyl hydrazide with phenyl hydrazine acetate and 30 pts water Fine yellow needles (from water) De composed on fusion It is extremely like the di phenyl hydrazide of dextro mannose, lævulose, and dextrose It, however, turns the ray of polarised light strongly to the right (Emil Fischer, B 23, 373)

Isomannitose, a sugar obtained, together with glucose, by boiling salep with acids, is probably identical with mannose (Tollens, B 21, 2150) Its phenyl hydrazide C₁₂H₁₈N₂O₅ [188°] is sl sol alcohol

Seminose, obtained by digesting with dilute H.SO, the cel ulose composing the thick walled cells of the endosperm of vegetable avory nuts, is identical with mannose (Reiss, B 22, 609, Schultz, B 22, 1192, Fischer a Hirschberger, B 22, 3218)

'Mannose carboxylic acid' C,H,,O. 16. $C_eH_{13}(CO_2H)O_e$ From mannose (50 g) by dis solving in water (250 g) and adding anhydrous HCy (18 c c) and a few drops of ammonia After three days the mixture is heated to 50° for 4 hours. The product appears to contain the ammonium salt of the acid and its amorphous a nide [183°], which may be ppd by alcohol (Fischer a Hirschberger, B 22, 365) The acid changes to anhydride when set free from In preparing the lactone (v infra) an acid [c 169°], probably the free mannose carboxylic acid, is sometimes formed

Salts -BaA', Obtained by boiling the ammonium salt with baryta Colourless, semicrystalline mass, m sol hot, v sl sol cold, water, insol alcohol Boiling cone HIAq re-

duces it slowly to n heptoic acid

Lactone $C_7H_{12}O_7$ [150°] Obtained by decomposing a hot solution of the Ba salt with the theoretical quantity of H₂SO₄ N sol water, m sol alcohol, insol ether Needles, v.

Phenylhydraside C,H,,O,N,H,Ph [220°-3°] Formed by boiling the Ba salt with aqueous NaOH, and adding HOAc and phenyl hydrazine acetate (Fischer a Passmore, B 28, 2732) Very small prisms, sol hot water Decomposed on fusion

MANTLE MUCIN v PROTEIDS, Appendix O. MARGARIC ACID C17H24O2 (Heptadecore acid) Mol w 270 [60°] The name margaric acid was originally applied to an acid C1,H34O2 sup posed to occur in the product of the saponifica tion of solid natural fats, but this acid was shown by Heintz to be a mixture of palmitic acid C16H32O2 and stearic acid C18H36O2 An acid C1,H3,O2 occurs, however, according to Ebert (B 8,775), in adipocere, a substance formed in dead tissues of animals Formed by boiling its nitrile (cetyl cyanide) with alcoholic potash (Heintz, P 102, 272) White crystals —BaA', white amorphous powder -AgA' white amorphous powder

Nutrule C_{1e}H_{ss}CN [58°] (?) (Köhler, J 1856, 579, cf Becker, A 102, 21d) According to Heintz (J 1857, 445), margaronitrile prepared from potassium cetyl sulphate and KCy is an

Margaric acid C₁₆H₃₃ CO₂H [60° uncor.]. (277° at 100 mm) Prepared by the oxidation

of methyl-heptadecyl-ketone (Krafft, B 12, 1672)

Probably identical with the preceding acid
MARJORAM OIL S G 1= 911 (Bruylants) The essential oil obtained by steam distillation from the flowers of sweet marjoram (Majorana hortensis or Origanum majorana) Yellow oil which becomes brown on standing. It has a pungent smell, a hot peppery taste, and an acid reaction According to Bruylants (J Ph [4] 30, 33, cf Mulder, A 31, 69) it begins to boil at 185° and the thermometer remains stationary at 215°-220° Bruylants found it to consist of 5 pc of a dextrorotatory terpene, 85 pc of a mixture of dextrorotatory camphor and borneol, According to Kane (A 32, and 10 pc of resin 285) the essential oil of wild marjoram (Origanum vulgare) contains a terpene which boils at 161° and has SG 867 According to Beilstein a Wiegand (B 15, 2855) oil of sweet marjoram contains a terpene $C_{10}H_{16}$ (178° 1 V) SG 185 846, which absorbs HCl, forming liquid C10H18HCl By distilling the oil of marjoram over sodium Beilstein a Wiegand obtained liquid C15H26O (200°-220°)

Cretan oil of marjoram from Origanum hirtum has S G 15 951, and 100 mm produce a rotation of -04° It contains 50 pc of carvacrol [2°] and dissolves in half its volume of 15 pc soda solution (Jahns, Ar Ph [3] 15, 1, 16, 277) The oil also contains a mixture of terpenes, and a phenol that is coloured violet by FeCl, found a little carvacrol in the oil from Ori

ganum vulgare

[160°] The bitter principle MARRUBIIN of white horehound (Marrubium vulgare) (Kro mayer, Ar Ph [2] 108, 257, Harms, J 1863, 593) Prepared by exhausting the dried herb with hot water, evaporating, and extracting with alcohol Large tables (from ether) or needles (from alcohol) Almost insol cold, sl sol hot, water Not affected by alkalıs Metallic salts do not ppt it Not ppd by tannin Hot conc HClAq does not affect it Conc H,SO, gives a brownish yellow solution Cold HNO, has no action, hot HNO, forms a yellow solution

MARSH GAS v METHANE

MARTYLAMINE v p Amido diphenyl.

MASOPIN C22H36O [155°] Occurs in a resin used in Mexico for chewing, said to be the dried juice of a tree called Dschlite resin occurs in porous lumps, smelling like rotten cheese, but with little taste The masopin is obtained by boiling the resin with water, and crystallising the residue from alcohol (Genth, A White silky needles (from ether) 46, 124) After fusion, it melts a second time at 70° distillation it yields a terpene and a crystalline acid, of which the Ag salt contains 45 5 pc of

MASTIC A resin obtained by incisions in the bark of Pistacia lentiscus, a tree growing in Chios Small round transparent grains with Used for making var faint agreeable odour nishes and, from the earliest times, for chewing Softens when masticated S G 1074 Aqueous alcohol dissolves the greater part C₄H₄₅O₄, leaving masticin C₄₄H₄₇O₂ undissolved (Johnston, P T 1839, 182) Fluckiger (Ar Ph. 219, 170) found 2 p c of a dextrorotatory terpene in mastic.

MATEZITE C, H, O, [187°] $[a]_D = 64 \text{ T}$ Occurs in Madagascar caoutchouc (mateza rori tina) (Girard, Bl [2] 21, 220, C R 110, 84) Identical with (3) Pinite (Combes, C. R 110, 46). Crystalline nodules, v e sol water, m sol alco hol Sublimes above 200° Resembles dambonite but is dextrorotatory Fuming HIAq splits it up on heating into McI and matezo dambose $C_0H_{18}O_9[246^\circ][\alpha]_D=67.6$, which is dextrorotatory and more soluble in water than dambose Matezo dambose is identical with the (β) inosite of Maquenne (C R 109, 812) It forms small tetrahedra when ppd by adding alcohol to its aqueous solution

MATICIN A bitter substance which remains dissolved in the water in the retort in the preparation of the essential oil of matico by distilling the leaves of Piper asperifolium with steam It is sol water and alcohol, and insol ether (Hodges,

P M [3] 26, 204, C S Mem 1, 123) Its solution is not ppd by lead acetate MATICO-CAMPHOR $C_{12}H_{20}O$ [94°] Occurs in the essential oil of matico leaves (Piper angustifolium), from which it is obtained by distilling off the greater part and allowing the residue to crystallise (Kugler, B 16, 2841) Hexagonal crystals V sol alcohol, ether, benzene, petroleum ether. &c With HCl it gives a violet colour, passing into blue, and finally becoming green. H2SO, colours it yellow, then red, and lastly violet A mixture of H,SO, and HNO, first produces a yellow, which then becomes violet, and finally a splendid blue

MAUVANILINE C. H., N. A by product in the preparation of rosaniline by the oxidation of crude aniline (De Laire, Girard a Chapoteaut, C R 64, 416, Bl [2] 7, 366), cf Girard a Pabst, Bl [2] 34, 37) Light brown crystals (containing aq, which is given off at 130° with decompo sition) Insol cold, v sl sol hot, water, sol alcohol, ether, and benzene Its salts form lus trous bronze green crystals, v sl sol cold water, Trı ethyland dye silk and wool mallow red mauvaniline C19H1, Et3N, dyes bluish violet, while tri phenyl mauvaniline C, H, Ph, N, is a blue dye

The first aniline dye MAUVEINE C₂₇H₂₄N. The first amline dye introduced (Perkin, 1856) Obtained by adding a cold dilute solution of a salt of crude aniline to a cold dilute solution of K₂Cr₂O, and leaving the mixture to stand for 12 hours The resulting black pp is dried, extracted with benzene, dissolved in alcohol, and the filtrate evaporated When aniline sulphate is used the product is (C₂,H₂,N₃,SO₄, aniline hydrochloride yields C₂,H₂,N₄Cl (Perkin, A 131, 200, C J 35, 717) On adding aqueous KOH to a solution of a salt of mauveine the base separates as a violet black crystalline substance It dissolves in alcohol, forming a violet solution, which on addition of acids turns purple Mauveine is insol benzene and ether With dilute acids it forms purple solutions, with stronger acids, blue Conc H2SO4 forms a dirty green solution Dyes silk mauve Used for postage stamps Oxidised by PbO, and boiling HOAc it gives para safranine C20H18N4

-B'HCl tufts of small prisms with Salts green metallic lustre Insol cold, sl sol hot, water, m sol alcohol, nearly insol ether—
"B'H,Cl, blue, with coppery lustre Unstable.
Becomes B'HCl when dissolved in alcohol—

green crystalline powder, v sl sol B' H,PtOl slcohol -B'H2PtCl₆ blue -B HAuCl₄ -B'HBr -B'Hl lustrous prisms -B'₂H₂SO₄ -B'H₂CO₃ prisms, with green metallic lustre On boiling prisms, with green metallic lustre

its solution CO2 is given off

Ethyl mauveine C₂₇H₂₃EtN₄ Formed by heating mauveine with EtI at 100° Its colour is redder than that of mauveine During the manufacture crystals of $C_{27}H_{28}EtN_4HI_8$ sometimes ap pear $-C_{27}H_{28}EtN_4HCl$ Forms a reddish purple solution in alcohol - (C2,H2,EtN,HCl)2PtCl4

Golden green lustre

Pseudo-mauveine C₂₄H₂₀N₄ (Perkin, C. J 35, 5) Present in commercial mauveine It is 725) more soluble in alcohol than mauveine strong base, and dyes silk almost exactly like mauveine Pure aniline gives pseudo mauveine on oxidation, hence it does not contain methyl Mauveine is probably derived from aniline and p toluidine The violet colouration given by bleaching powder to a dilute solution of aniline is probably due to pseudo mauve-ine —C₂H₂N₄HCl Greenish-golden lustre —

(B'HCl), PtČl, MAYER'S REAGENT v Alkaloids, Re-

action 3

MAYNAS RESIN Calaba or Galba of the Antilles (Lewy, A Ch [3] 10, 380) A resin extracted by mension from Calophyllum calaba Alcohol extracts from it $C_{14}H_{18}O_4$, which sepa rates on cooling in yellow monoclinic prisms Maynas resin is insol water, but v sol KOHAq and ammonia It melts about 105°

MECCA BALSAM Balm of Grlead produce of Balsamodendron grieadense, a shrub growing in Arabia Felix. There appear to be several varieties of it It contains a fragrant volatile oil, an acid resin sol alcohol, and a resin, insoluble in alcohol (Bonastre, A 3, 147, Trommsdorff (Trommsd Neues Journal, 16, 62)

MECONIC ACID C,H,O, 3aq, te C₅HO₂(OH)(CO₂H)₂ Mol w 200 S 25 at 100° Heat of neutralisation (4 mols NaOH) 87,382 (Gal a Werner, Bl [2] 47,162) Electrical conductivity Ostwald (J pr [2] 82,368) Occurrence — In opium (Sertumer, Am S 55,

72, 57, 183, 64, 65, Robiquet, A Ch 5, 282, 51, 236, 53, 425, Liebig, A 7, 87, 26, 113,

Preparation —Opium is exhausted with water at 38°, the extract is neutralised with CaCO, evaporated to a syrup, and mixed with a concentrated solution of CaCl2, which ppts calcium meconate The pp (1 pt) is suspended in conc HClAq (3 pts) mixed with boiling water (20 pts), and kept near 100° till dissolved On cooling, acid calcium meconate separates in crystals These (1 pt) are again dissolved in a mixture of HClAq (3 pts) and boiling water (20 pts), and, on cooling, meconic acid separates (Gregory, A 24, 43) It may be further purified by crystallising its ammonium salt from water (How, A 83, 850)

Properties - Micaceous scales or small trimetric prisms (containing 3aq) (Burghardt, C J 27, 937) It gives off its water of crystallisation at 100°, then becoming a white opaque mass Has a sour taste and strongly reddens litmus Sl sol cold water, v sol alcohol, sl sol ether FeCl, colours its solutions blood red This This colouration, like that with sulphocyanides, is

much weakened by oxalic acid and by metaphos phoric soid (Dupré, C N 32, 15), but it is not destroyed by boiling or by dilute HClAq conic acid may be regaided as a derivative of the hypothetical CH CH CH CH

Reactions -1, Heated at 120° it gives off CO2, and comenic acid C₅H₂O₂(OH)(CO₂H) remains At a higher temperature the comenic acid is further resolved, pattly into CO₂ and pyrome conic acid C₅H₃O₂(OH), and partly into water, acetic acid, and oily and carbonaceous products

When boiled with water or with HClAq it
gives CO₂ and comenic acid—3 Nitric acid
oxidises it, forming oxalic acid—4 Boiling cone KOHAq also yields oxalic acid -5 Boiling aqueous ammonia forms comenamic acid Comenamic acid yields C₅H₃NO(OH)CO₂H pyridine on dry distillation with zine-dust (Lieben a Haitinger, B 16, 1263) The comen amic acid is di oxy picolinic acid, and comenic acid is probably an intermediate product in its formation -6 Bromine, acting on its aqueous solution, forms a brominated comenic acid -7 Aqueous HI gives comenic acid —8 Sodium amalgam reduces it to hydro meconic acid -9 Gives with alcohol and HCl a di ethyl ether, C₂HO₂(OH)(CO₂Et)₂, whence a silver compound, C₂HO₂(OAg)(CO₂Et)₂, which gives with EtI a tri-ethyl derivative C₃HO₂(OEt)(CO₂Et)₂ [61°] This gives no colour with FeCl₃ (Ost a Mennel, J pr [2] 23, 439) -10 PCl, converts it into a liquid chloride, probably C₅HCl₅(COCl)₂, whence ice water forms 'chloro mecenic' acid, C.ClO(OH)(CO,H), aq [165°], whereas waim water forms only oxalic acid (Hilsebein, J pr [2] 32, 136) Chloro mecenic acid gives a green colour, with solution of ferric chloride. It forms an ether, C_ClO(OH)(CO_H)(CO_2Et), [148°], which gives an acetyl derivative O_ClO(OAc)(CO_2H)(CO_2Et), [70°] It also forms become acids. Chloro mecenic acid is decom barium salts posed by sublimation into carbonic acid and yellowish needles of pyro chloro mecenic acid, C_bH₂ClO(OH), aq [174°] The solution of this acid is turned dark green by FeCl, Its alcoholic solution turns the skin red It forms a crystal line calcium salt, (C,H,ClO2),Ca Chloro mecenic acid dissolves in cone NH,, the solution turning successively red, violet, and blue, owing to the formation of two nitrogenous colouring matters, 'mecenic blue' and 'mecenic red' mecenic acid is reduced by treatment with sodium amalgam, forming di-hydro chloro mecenic acid $C_bH_2ClO(OH)(CO_2H)_2$, [145°] Fuming HI at 100° reduces chloro mecenic acid to an oxy pentane di carboxylic acid, C₃H₁₀O(CO₂H)₂
This body forms groups of needles [149°] Its
silver salt, Ag₂A", is a crystalline powder, insol
water Its barium salt, BaA", forms white
prisms Its ether, Et₂A", is an oil, boiling about (250°) Oxy-pentane di carboxylic acid, about (200') CAy-pensane when distilled with lime, yields amyl alcohol, (c 130°) (Hilsebein J pr [2] 32, 129-158)
Salts—(NH,)H₂A" aq granular crystals, sl sol water—(NH,)₂HA" xaq slender needles

-A barium salt is ppd by adding BaCl₂ to a solution of an alkaline meconate, in white flakes, soluble in acetic acid — CaH,A", 2aq ppd by adding CaCl₂ to aqueous meconic acid — CaHA" aq yellow gelatinous pp, formed by adding CaCl, to a solution of ammonfum meconate -The cupric salts are green pps -Pb,A", 2aq white flocks, ppd by adding lead acetate to a solution of meconic acid (Sten house, A 51, 231) -A sparingly soluble ferric salt may be obtained by the action of ferric sul phate on ammonium meconate (Stenhouse) Fe₂Ca₃A'''₄ 5aq (Rennie, C N 42, 75) —Ag₂HA''' white pp got by adding AgNO, to a solution of meconic acid -Ag.A" yellow pp from ammo nium meconate and AgNO, -Aniline salt (C_aH_aNH₂)₂C₇H₄O₇ arystalline (Korff, A 138, 195)—Urea salt (CON₂H₄)₃C₇H₄O₇ (Hlasi wetz, J 1856, 699)—Narceine salt [126°] from narceine (1 mol) and meconic acid (1 mol) Lemon yellow crystals, sol hot water (Merck, C C 1889, 384) -The acid morphine salt could not be obtained by Dott (Ph [3] 17, 690) It will be observed that meconic acid has but little tendency to form tribasic salts, so that it might perhaps be more correctly regarded as a dibasic acid (cf Dittmar a Dewar, Pr E 1867, Dott, Ph [3] 11, 576)

Ethyl derivative C₅HO₂(CO₂H)₂(OEt) [200°] Formed by boiling C₅HO₂(CO₂Et)₂(OEt) for forty eight hours with water, and evaporating the solution Small prisms grouped in lumps Decomposed by fusion Gives no cclour with FeCl₃ Gives, with most metallic salts, no pp Lead acctate is an exception Heated alone till it melts, CO₂ is given off, and the ethyl derivative of comenic acid formed Its aqueous solution is converted by bromine into a brominated derivative of comenic ether —PbA" 1½aq Crys-

talline pp

Mono ethyl ether

C₃HO₃(CO.Łt)(CO,H)(OH) [179°] Prepared
by dissolving meconic acid in alcohol, heating
to 100°, and subjecting to a current of HCl
till crystals begin to appear The liquid on
cooling deposits crystals of the mono ethylic
ether (E Mennel, J pr [2] 26, 450) It
gives a red colour with FeCl₃—Silver salt
C₃HO₂(CO,Et)(CO,Ag)(OH)₂aq—Barium salts
BaC₆H₆O, and Ba(C₆H,O)₂

Dr ethyl ether C₃HO₂(CO₂Et)₂(OH) [112°] Prepared by passing HCl into an alco holic solution at 100° until the crystals (of mono ethylic ether) which are first formed are dissolved up again. On pouring into water, plates of the di ethylic ether separate (How, A 83, 350, Mennel, J pr [2] 26, 453) Plates From dilute solutions it crystallises with laq as needles. Gives a red colour with FeCl₃. An amorphous pp is formed by adding AgNO₄ and then exactly neutralising with NH₃—NH₄C₁₁H₁₁O₇, needles (from alcohol), v sol water. Its solution is ppd by various metallic salts.

Ethyl derivative of the diethyl ether C₅HO₂(CO₂Et)₂(OEt) [61°] From C₅HO₂(CO₂Et)₂(OAg) and EtI Gives no red colour with FeCl₃ Boiled with water it changes to the ethyl derivative of meconic acid (q v)

Not acted upon by bromine

Mono-amide
C₂HO₂(CONH₂)(CO₂H)(OH) aq Meconamic acid
From the above by the action of aqueous NH₂,
followed by HCl Crystallises in hard lumps
from water Not decomposed by cold NaOH,
converted by boiling NaOH into meconate
Copper salt C₂H₂O₂Cu 2sq

Basic ammonium salt of amide C₂HO₂(CONH₂)(CO₂NH₃)(ONH₄) This yellow pp is the first product of the action of NH₂ upon mono ethylic meconate

Di amide C₂HO₂(OH)(CONH₂)₂ From the diethyl ether and boiling aqueous NH₃ (How)

Powder, sl sol cold water

Oxim C,H,O,NH Formed by treating me conic acid with hydroxylamine hydrochloride (Odernheimer, B 17, 2081) Small colourless needles (containing H,O) V sol water, sl sol alcohol, ether, and chloroform, insol ligroine Decomposes suddenly at 190° It gives a red colour with Fo,Cl₆ It reduces Fehling's solution By boiling with HCl hydroxylamine is split off —A"Na₂ colourless crystals —A"Ag, aq white sparingly soluble pp—A"Ba 10aq sparingly soluble concentric needles —A"Ca 2aq. sparingly soluble needles

Hexahydride CH₁₀O, Hydromecome acid Obtained by reducing meconic acid suspended in water by adding sodium amalgam (Korff, A 138, 191) Separated by decomposing the lead salt by H₂S and evaporating the filtrate Strongly acid syrup, v sol water, m sol alcohol, insol ether Ppd as deliquescent flocks on adding ether to its alcoholic solution Not affected by HI Gives no colour with FeCl₂—BaA" 2aq amorphous pp, sol water, insol alcohol — PbA" 1½aq amorphous pp—Ag,A" ½aq white granular pp

Reference -Pyromeconic acid and Pyrome

CAZONIC ACID

MECONIDINE C₂₁H₂₃NO₄ [58°] An alkaloid contained in the aqueous extract of opium (Hesse, A 153, 47) The aqueous extract is ppd by Na₂CO₃, the pp dissolved in ether, the ethereal solution shaken with dilute acetic acid, and the acid solution poured into aqueous NaOH After 24 hours the pp of thebain and papaverine is removed by filtration, the filtrate neutralised by HCl, rendered alkaline by NH3, and shaken with chloroform The chloroform is then shaken with acetic acid, and the acid solution exactly neutralised by ammonia, which ppts lanthopine The filtrate is mixed with KOH and shaken with Codanine and laudanine separate, and the mother liquor is then shaken with dilute acetic acid, the solution saturated with NaCl, the ppd meconidine hydrochloride decomposed by NaHCO, and the base extracted with ether and dried at 90°

Properties — Brownish yellow transparent amorphous mass Cannot be sublimed Tasteless Insol water, v sol alcohol, ether, benzene, chloroform, and acetone Its alcoholic solution turns red litmus blue Sl sol NH,Aq, v sol NaOHAq Can be extracted by ether from its solution in ammonia but not from that in caustic soda Its solution in dilute H₂SO₄ becomes rose coloured in a few minutes, and purple red on standing for sometime, or immediately on boiling Conc H₂SO₄ gives an olive-green solution Conc HNO₃-colours it orange red The dilute solutions of the salts have an intensely bitter taste — B'₂H₂PtCl₆ yellow amorphous pp which soon turns reddish The aurochloride is a dingy yellow amorphous pp

MECONIN $C_{i_1}H_{i_0}O_{i_2}$ a.e $C_{e}H_{2}(OMe)_{e} < \stackrel{CH}{CO}>O$. [1.6.3]? Anhydride of

108 MECONIN.

Meconomo acid. Opennyl Mol w 194 [99°] (M a F), [102 5°] (Wegscheider, M 3, 351, Prinz, J pr [2] 24, 371) S 4 in the cold, 5 at 100° A neutral substance existing in opium (Dublanc, A Ch [2] 49, 17, Couerbe, A Ch 49, 11, 50, 337, 59, 148) It may also be extracted by either from the root of Hydrastis canadeness (Freund, B, 22, 459)

densis (Freund, B 22, 459)

Formation—1 Together with cotarnine, opianic acid, and hemipic acid, by the action of warm dilute nitric acid on narcotine (Anderson, Tr E 20, 347, 21, 204)—2 From opianic acid by the action of sodium-amalgam, or of zinc and H.SO. (Matthiessen a Foster, C J 16, 849)—8 Together with hemipic acid by the action of caustic alkalis on opianic acid (M a F)

Preparation -1 A concentrated aqueous extract of opium is ppd by dilute ammonia, and the filtrate evaporated to crystallisation crystals are extracted with alcohol, which after evaporation deposits crystals of meconin, which are recrystallised from water and ether suc cessively (Couerbe) -2 The aqueous extract of opium is precipitated by chloride of calcium, the precipitated meconate of calcium is filtered, the filtrate evaporated to the crystallising point, and separated from the deposited hydrochloride of morphine, and the dark mother liquor is diluted with water, filtered from the flocks which separate, and treated with ammonia, which pre cipitates narcours, thebaine, and a large quantity of resin The filtrate is mixed with acetate of lead the excess of lead is removed from the filtered liquid by dilute sulphuric acid, and the filtrate is neutralised with ammonia, and evaporated to the crystallising point at a moderate heat, whereupon narceine separates out, and then sal ammoniac by further concentration mother liquor is repeatedly digested with } vol ether at 26°, and the ether is distilled off from the extracts, a brown syrup then remaining On treating this syrup with dilute hydrochloric acid, papaverine dissolves, and meconin remains in the form of a dark-grey crystalline powder, which, to free it from resin and purify it com-pletely, must be several times crystallised from boiling water, with addition of animal charcoal (Anderson)

Properties — Colourless hexagonal prisms Appears tasteless at first, but afterwards acrid May be sublimed SI sol cold water, m sol alcohol and ether Sol KOHAq, nearly insol NH,Aq Inactive Its aqueous solution ppts lead subacetate but not lead acetate Dilute H,SO, forms a colourless solution which becomes dark green when evaporated (Couerbe) Conc H,SO, forms a colourless solution which becomes purple on heating

Reactions—I Cone HClAq at 100° gives MeCl and methyl normeconin C₅H₅O₄ (M a F) HI acts in like manner—2 Baryta water dissolves meconin forming 'barium meconinate' (C₅H₄(OMe)₅(CH₄OH) CO₂)₂Ba This salt crystal lises in needles, but the free acid splits up at once into water and its anhydride meconin (Hessert, B 11, 240, Prinz, J pr [2] 24, 373) B Potash-fusion forms methyl-normeconin C₅H₂O₄ [125°] and, finally, protocateching acid Cyndised by MnO₅ and dilute H₂SO₄ to opianic acid.—5. KMnO₄ oxidises it to hemipic said [180°].

Chloro-meconin $O_{10}H_0\text{ClO}_4$. [175°] Obtained by passing chlorine into a cold saturated aqueous solution of meconin (Anderson, A 98, 47) Colourless needles May be sublimed Sl sol cold water, v sol alcohol and ether Hot $H_2\text{SO}_4$ gives a greenish blue colour

Bromo-meconin C₁₀H₂BrO₄ [167°] (Ander son), [177°] (Salomon, B 20, 888) From me conin and bromine water Colourless needles,

sl sol water
Indo-meconin C H IO [11

Iodo-meconin C₁₀H₉IO₄ [112°] From me conin and chloride of iodine (A) Needles, nearly insol water, m sol alcohol and ether

Nitro-meconin C₁₀H₉(NO₂)O₄ [158°] Frommeconin and HNO₃ White needles (from alcohol)

Amido-meconin C₁₀H₂(NH₂)O₄ [171°] Obtained by reducing nitro meconin with iron and acetic acid (S) M sol hot benzene

Methyl-normeconin C,H,O, ve

 $C_eH_2(OH)(OMe) < CH_2 > O$ [125°] Obtained

by heating meconin with cone HClAq (Matthiessen a Foster), by heating meconin with KCy at 180° (Bowman, B 20, 890), or by potash fusion from meconin or narcotine (Beckett a Wright, J 1876, 810) Monoclinic prisms, v sol hot water and alcohol, sl sol ether FeCl, colours it blue It reduces silver salts in the cold Potash fusion converts it into protocatechuic acid—CaA'₂—BaA'₂

Meconin acetic acid C12H12O : e

C₆H₂(OMe)₂COO [167°] Obtained

by heating opianic acid with a mixture of malonic acid, acetic acid, and sodium acetate for 10 hours at 100° (Liebermann a Kleemann, B 19, 2290) Glistening needles By boiling with baryta water it is converted into opianyl acetic acid C₆H₂(OMe). (CO₂H) CH(OH) CH CO₃H By heating with HI it is dimethylated, giving

C_sH₂(OH)₂CO CH CH₂CO H ethyl ether melts at 131⁶ [228°], of which the

Salts -A'Ag white slightly soluble crystals $-A'_2Ca$ needles, al. sol water $-A'_2Cu^{\times}$ blue crystalline pp

Methyl ether A'Me [124°], glistening plates

Ethyl ether A'Et [83°], plates, sol alcohol, ether, and hot water

Nitro meconin acetic acid

CO C_oH(NO₂)(OMe)₂ O [176°] Nearly CH CH₂ CO₂H colourless crystals Obtained by nitration of meconin acetic acid It dissolves in cold H₂SO₄ with a yellow colour, which becomes red on warming from formation of an indigo derivative By tin and HCl it is reduced to the lactone of

(Py 1 3)-di-oxy-(B'2.3) di methoxy-di hydro-

Salts —A'2Ca. yellow needles.--A'Ags; curdy pp.—A'2Cux; green pp

Ethyl ether AEt [129°], glistening | in 50-75 pc acetic acid. It contains 59 pc of needles, insol water, sol alcohol and benzene | sulphur and 2 pc Fe (Liebermann & Kleemann, B 19, 2295)

 ψ Meconin $C_0H_2(OMe)_2 < CH_2 > O [16\frac{2}{3}]$? De methyl derivative of de oxy phthalide [124°] When hemipimide, the imide of hemipic acid C.H.2(OMe)2 CO NH, is heated with tin and hydrochloric acid it is red seed to hemipimidine $C_6H_4(OMe)_2 < \stackrel{CH}{CO}^2 > NH$ [181°], which yields a

nitroso derivative • C₆H₂(OMe)₂<CH₂>N NO [156°], which on treatment with dilute NaOH in the cold yields pseudo meconin (Salomon, B Obtained also by boiling hemipimide with zinc dust and acetic acid Long colourless needles (from water) Sl sol cold water, sol benzene, alcohol, and ether Unlike meconin it is not affected by boiling with dilute H SO, and MnO. Dilute HNO, at 150° forms nitro hemipic acid and nitro ψ meconin, whereas meconin yields only nitro meconin Fusion with KOH or KCy does not affect ψ meconin

Brome \(\psi \) meconin C₁₀H₀BrO₄ [142°] From \(\psi \) meconin and bromine White flocculent pp,

sol benzene, msol petroleum

Nitro \(\psi\) meconin C₁₀H_n(NO₂)O₄ [166°] From \(\psi\) meconin and fuming HNO₄ Yellow needles, which yield oxalic acid on further treatment with nitric acid

Amido ψ meconin $C_{10}H_9(NH_2)O_4$ [165°] Ob tained by reducing the preceding More basic

than amido meconin

MECONOISIN C₈H₁₀O₂ [88°] S 37 Oc curs in opium, and found in the mother liquor after separation of meconin When this is allowed to stand, crystals are deposited, which are washed with alcohol and recrystallised from water (T a H Smith, Ph [3] 8, 981) Large, leaf shaped crystals, v e sol hot water It gives a green colour when heated with dilute H.SO

MEDULLIC ACID C₂₁H₄₂O₂ [72 5°] A fatty acid said to be produced, together with stearic and palmitic acids, by the saponification of beef-

marrow (Eylerts, Ar Ph [2] 104, 129) MELAM v CYANIC ACIDS

MELAMINE v Cyanuramide in the article CYANIC ACIDS

MELAMPYRITE v DULCITE

MELANILINE v DI PHENYI GUANIDINE

MELANIN C 60, H 48, N 108, ash 22 A black pigment covering the choroid membrane of the eye (Scherer, A 40, 63) Insol water, alcohol, and ether

Phymatorhusin C 557, H 60, N 123, S 8 to 9, Fe 07 to 2 A pigment occurring in melanotic urine and tumours It is obtained by ppg with baryta, dissolving in Na,CO₃, and ppg with dilute H,SO₄ (Berdez a Nencki, *J Th* 1886, 477, Mörner, *H* 11, 81) It is a brownishblack amorphous powder, insol water, alcohol, ether, chloroform, and dilute mineral acids, v e sol ammonia, aqueous NaOH, Na2HPO4, and Na₂CO₂ Ppd from its solution in NaOH by baryta, MgSO₄, and BaCl₂ With potash fusion it gives skatole, volatile fatty acids, nitriles, KCy, and K₂S Hot H₂SO₄ forms pyridine Phymatorhusin is accompanied by another black substance, which differs from it in being soluble

C 535-556, H 27-89, Hippomelanin N 105-109, S 28-30 Occurs in melanotic tumours of horses May be obtained by diluting the emulsion of a melanotic spleen with water The pp 18 and adding CaCl₂ and Na₂HPO₄ washed at 40°, and then treated with a digestive fluid until the solution ceases to give a reaction for peptones The residue is washed with aqueous soda, alcohol and ether (Miura, C C 1887, 250). Brownish black powder, insol water, alcohol, and ether Dissolves on warming in dilute acids and alkalis Potash fusion gives KCy, succinic acid, formic acid, and hippomelanic acid Hippomelanic acid is a black amorphous body, sol ammonia, and reppd by HCl It contains less S and more C than the melanin (Nencki a Sieber, C C 1888, 587) The black pigment in dark hair and in bird's feathers after purifying by al coholic NH, and dilute H SO, may be represented by the formula $C_{18}H_{16}N_2O_8$ (Hodgkinson a Sorby, J 1876, 936) Black powder Not affected by dilute acids and alkalis

Sepiaic acid C 563, H 36, N 123, S 5, 0 27 2 Obtained by digesting the pigment from the ink bag of sepia with 15 pts of 10 pc Sol alkalis, ppd from ammoniacal potash solution by ammonia zinc chloride or copper

sulphate (Nencki a Sieber)

MELANTHIN C₂₀H₃₃O, [205°] Occurs in the seeds of Nigella sativa (Greenish, Ph [3] 10, 909, 1013) Prepared by extracting the seeds with alcohol, evaporating the extract, dissolving the pp in alcohol, and fractionally ppg with water Minute grey crystals (from alcohol) Insol water, benzene, CS2, and light petroleum, v sol alcohol, sol alkalıs, sl sol chloroform Conc H₂SO₄ gives a red colouration H₂SO₄ and sugar give a violet blue colour Boiling dilute HCl splits it up into a sugar and melanthigenin C14H202, which forms minute crystals, sl sol. water

MELANURENIC ACID v AMMELIDE

MELEM v CYANIC ACIDS

MELENE C₃₆H₅₀ [62°] (370°-380°) S G 89 VD 10-118 S (alcohol) 13 in the cold, 3 6 at 78° An olefine (?) produced by the dry distillation of bccs' wax (Lttling, A 2, 252, Lewy, A Ch [3] 5, 395, Brodie, A 71, 156)— White nacreous plates (from ether) Insol water, sl sol cold alcohol, v sol ether Not attacked by cold H_2SO_4 , slightly attacked by boiling HNO. Attacked by chlorine MELEZITOSE $C_{12}H_{22}O_{13}$ [148°] [a]_D=94°

(B), 88 5° (V) A sugar discovered by Bonastre in the manna of Briancon which exudes from the young branches of 'mélèze' (Pinus Larix) (Berthelot, A Ch [3] 55, 282) It occurs also in 'taranjobine' or Turkestan manna (Villiers, Bl [2] 27, 98, Alekhine, Bl [2] 46, 824) tained by extracting the Briancon manna with boiling alcohol, and evaporating After a few weeks melezitose separates, it is then recrystallised from alcohol Monoclinic crystals containing aq (V), or anhydrous crystals (A) About

Dextrorotatory V sol water, nearly insol cold, sl sol boiling, alcohol, insol ether Its aqueous solution is ppd by ammoniacal lead acetate Boiling dilute H.SO. forms glucose It is turned brown by alkalis. It does not reduce Fehling's solution Does not ferment with yeast It forms a compound with phenyl hydrazine It gives an octo acetyl derivative.

MELIDO-ACETIC ACID C, H, N,O, 26 (CN), N, H, CH, CO, H Formed by treating cyanamide with chloro acetic ether and NaOEt (Drechsel, J pr [2] 11, 332) Amorphous mass, but obtained in a crystalline state by ppg its ammonium salt with HCl Decomposed by heat without previous fusion Insol alcohol and ether, v sl sol cold water Sol aqueous HClAq, baryta, and KOHAq, but insol NH, Aq -HA'HCl needles, sl sol cold water— HA'HNO,Aq—AgA'HNO,Aq—(HA'),H,SO,4aq MELILOTIC ACID v OXY PHENYL PROPIONIC

MELILOTOL $C_{18}H_{16}O_5$ (?) An oil found, together with coumarin, in the yellow melilot (Melilotus officinalis) Extracted by distilling the plant, when in flower, with steam, and ex tracting the distillate with ether (Phipson, C N 32, 25, C R 86, 830) Liquid, v sl sol water, alcohol, and ether Has an agreeable odour When boiled with cone KOHAq it yields oxy phenyl propionic (melilotic) acid C₂H₁₀O₃ Melilotol is perhaps identical with the lactone of

CH, CH, melilotic acid C_sH₄< O CO

MELINOIN - TRI - SULPHONIC ACID

 $\mathbf{C_{34}H_{17}O_3(SO_3H)_3}$

Formation -1 By warming a mixture of p oxy benzoic aldehyde, (β) naphthol, and H₂SO₄
2 From benzoic aldehyde, (β) naphthol, and H₂SO₄—3 By heating Baeyer's condensation product C₃₄H₂₆O₃ (from benzoic aldehyde and (8) naphthol) with H_2SO , (Trzcinski, B 16, 2835, 17, 500) — Yellow crystalline powder Insol absolute alcohol, tolerably sol water, the dilute solution being of a rose red colour with a It dissolves in strong green fluorescence H₂SO₄ or HNO₃ with a splendid green fluor escence, and is not attacked even on boiling It forms unstable compounds with HCl and H2SO4, although it is itself a strong acid

Salts -A"K, easily soluble fine colourless needles -A", Ca, aq colourless soluble crystals -A"2Ba, sparingly soluble white amorphous

pp or microscopic needles

MELISSIC ACID C.0H.00, 1 e C.1H.00C0, H, or C.1H.0C0, 1 e C.2H.0C0, H [90°] Occurs in bees' wax (Nafzger, A 224, 225) Formed by heating the myricyl alcohol of bees' wax with soda lime at 270°-300° in absence of air (Brodie, 4 71, 156, Von Pieverling, A 183, 344, Sturcke, A 223, 295, Schwalb, A 235, 106) Sol alco scales, composed of minute needles hol, light petroleum, chloroform, and CS2, sl sol According to Schalfeeff (B 12, 697) melissic acid is a mixture of acids

Salts —PbA'₂ [119°] Insol alcohol and ther, sl sol boiling toluene, chloroform, and glacial acetic acid — MgA'2 — CuA'2 — AgA'

[95°], amorphous pp

Methylether MeA' [71°] Needles (from

ligroin)

Ethyl ether EtA' [70°] (Schwalb), [73°] (P) Needles (from alcohol) Split up on heating into ethylene and the free acid

Isoamyl ether C,H,A'. [69°].

MELISSYL ALCOHOL & MYRICYL ALCOHOL. MELITOSE v RAFFINOSE and SUGARS

MELLITIC ACID C₁₂H₈O₁₂ ie C₂(CO₂H)₈.

Mellic acid Benzene hexa-carboxylic acid.

Mol w 342 H C v 790,800 H C p 788,200

H F 546,800 (Stohmann, Kleber, a Langbein, J pr [2] 40, 141) Heat of neutro 84,034 (Gal a Werner, Bl [2] 47, 162) Heat of neutralisation

Occurrence — As, aluminium mellitate in honey stone or mellite (Klaproth, A D 1799,

Bacyer, A Suppl 6, 1)
Formation —1 By the oxidation of hexamethyl benzene by cold alkaline KMnO, (Friedel a Krafts, A Ch [6] 1, 470) -2 By the oxidation of charcoal by KMnO₄ (Schulze, B 4, 802, 806) -3 By the electrolysis of acidified water or of KOH using a positive electrode of gas carbon (Bartoli a Papasogli, G 11, 468, C C 1881, 327) —4 In very small quantity by oxidis ing coal, animal charcoal, or lampblack by alkaline NaOCl (Bartoli a Papasogli, G 15, 446)

Preparation - Powdered honey stone is boiled with ammonium carbonate, ammonia is added, and the filtrate evaporated to crystallisa tion The ammonium mellitate is recrystallised with addition of a little ammonia, dissolved in water, ppd by lead acetate, and the pp decomposed by H.S (Wohler, A 37, 263, Schwarz, A

66, 47, Claus, B 10, 559)

Properties - Stellate groups of delicate silky needles (from alcohol), v sol water and alcohol Decomposed by heat into CO and pyromellitic acid $C_{10}H_0O_8$ (Erdmann, J pr 52, 432), which solidifies in the neck of the retort as a radio-When strongly heated with crystalline mass glycerin it yields CO2 and trimesic acid C9H6O6 When heated to redness with soda lime it yields benzene (Baeyer, A Suppl 7, 5) Not decom posed by boiling HNO, sulphuric acid, HIAq, chlorine, or bromine When its aqueous solution is electrolysed, CO, hydrogen, CO, and oxygen

are given off (Bunge, J/R 12, 421) Salts —(NH₄)₆C₁₂O₁₂ 3aq trimetric crystals (Schwarz, A 66, 47) Decomposed at 150° with formation of paramide and ammonium eu chroate -(NH₄)₂H₄C₁₂O₁₂ 4aq trimetric prisms From ammonio cupric mellitate and H2S -K₈Av1 9aq trimetric crystals -K₄H₂Av1 8aq - $K_2^*H_3A^{*1}$ and large prisms, more soluble in water than the normal potassium salt — $(K_3H_3A^{*1})_4(KNO_3)_3$ 9aq (?) —Na_3A^{*1}2aq needles (from a hot cone solution) — Na, Avi 18aq large striated triclinic crystals — Ba, Avi 3aq white gelatinous pp, changing to scales — Mg, Avi 18aq crystalline mass - Mg,(NH,)2Avi 15aq glassy prisms — $Zn_3A^{v_1}15aq$ — $Zn_2A^{v_1}9aq$ — $Mn_3A^{v_1}18aq$ minute needles, more sol cold than hot water S (hot water) 125 - Co. Avi 18aq minute prisms (from boiling water) —Ni₃A^{vi} 24aq v sl sol water —Al,Avi 18aq Mellite SG 16 SH 336 (Bartoli, G 14, 105) Occurs in lignite at Asten in Thuringia, Bilin in Bohemia, and near Walchau in Moravia Massive nodules Dimetric crystals a c=1 745—Fe, A viFe, O, 9aq minute lemon yellow crystals, v sl sol water -Cu, Avi 12aq From boiling mellitic acid and cupric acetate Amorphous pp , becoming crystalline — $Cu_2H_2A^{v_1}12aq$ — $Cu_2(NH_4)_2A^{v_1}12aq$. from curric sulphate and ammonium mellitate. -Hg, A^{vi} 6aq (dried at 100°), granular mass -

Hg, A^{vi} 6aq (dried at 100°) granular pp — Pb, A^{vi} (dried at 180°) bulky white pp — Pd, A^{vi} (A^{vi} 81, 164) — A^{vi} white crystals (Karmrodt, A^{vi} 81, 164) — A^{vi} white crystal into powder (Wöhler, A^{vi} 30, 1) — A^{vi} white crystal into powder (Wöhler, A^{vi} [187°] From silver mellitate and MeI (Kraut, J^{vi} 1862, 281, A^{vi} 777, 273) Plates H C 1,825,600 H F 487,400 (Stohmann, J^{vi} 274,0356) — Ethyl ether Et, A^{vi} [73°] Isoamyl ether (O,H,,), A^{vi} Onl

Isoamyl ether (C,H11),Avi Oil

Chloride C.(COCI). [190°] (Claus, B 10,) Formed, together with an oxychloride C12O8Cl2, from PCl5 and mellitic acid Hard vitreous prisms (from ether) Sublimes in lamine at 240° Slowly decomposed by water laminæ at 240° into HCl and mellitic acid

Tri imide C12H2N3O6 te

 $\mathbf{c}'\left\{<_{\mathrm{CO}}^{\mathrm{CO}}>\mathrm{NH}\right\}$ Paramide Formed, to-

gether with euchroic acid, by heating ammo nium mellitate at 160° as long as NH3 escapes Water extracts ammonium euchroate from the residue leaving paramide undissolved (Wohler, A 37, 268, Schwarz, A 66, 52) White amor phous powder, insol water and alcohol Sol H SO, but reppd by water Boiling with water slowly converts it into (NH4)3H3C12O12 Alkalis convert it first into euchroic and then into mellitic acid AgNOs forms in its ammoniacal solution a gelatinous pp which gives off NH, when heated, leaving Ag₃N₂C₁₂O₆. An ammoniacal solution of paramide dropped into HClA; gives a white crystalline pp called 'paramic

gives a wine crystainte processed parameter acid. $C_{12}H_0N_3O_7(?)$ or CO_2H CO_3 CO_4 CO_5 CO_5 CO

tic acid or ammonium mellitate (1 mol) with aniline (6 mols) at 160° for 7 hours (Hotte, J pr [2] 32, 238) White amorphous mass

 $\begin{array}{c} D_1 \text{ i mide } C_{12}H_4N_2O_8 \text{ i e} \\ (CO_2H)_2C_6 \left\{ \left\langle \begin{array}{c} CO \\ CO \end{array} \right\rangle NH \right\}_{r} \end{array}$ Euchroic

Prepared by heating ammonium mellitate at 160° for several hours, dissolving in water, and adding HCl to the hot solution. The crystals which separate on cooling are recrystallised from water (Wohler, P 52, 610, Schwarz, A 66, 49) Small prisms (containing 2aq), sl sol cold water Strongly acid Melts about 280° Euchroïc acid is not decomposed by boiling water or HClAq When a solution of euchroïc acid is treated with zinc the metal becomes covered with a dark blue deposit of 'euchrone' This deposit detaches itself when the zinc is immersed in dilute HClAq After drying, euchrone is a black mass which becomes colourless when heated in air, being re-oxidised to euchroïc acid Euchrone forms a deep purple solution in NH, Aq or KOHAq, but the solution is quickly decolourised by the When a solution of euchroic acid is electrolysed, the negative platinum becomes coated with the blue deposit

Salts - (NH₄)₂C₁₂H₂N₂O₈ white crusts -An acid ammonium salt separates from hot solutions in yellowish crystals—BaA"aq pale-yellow powder—PbA"aq—PbA"4aq—Ag₂A".

sulphur-yellow powder.

Hexahydride C.H. (CO.H). Hydromellithe acid Formed by treating an ammoniacal solution of mellitic acid with sodium amalgam. neutralising with acetic acid, ppg by lead acetate, and decomposing the pp with HS (Baeyer, A Suppl 7, 15) Formed also in the electrolysis of aqueous KOH with a positive electrode of carbon (Bartoli a Papasogli, C C 1881, 327) Hygroscopic syrup, v e sol water By heating with H₂SO₄ (5 pts) there is formed, together with CO₂ and SO₂, trimesic acid C₆H₄(CO₂H)₄, prehnitic acid C₆H₂(CO₂H)₄, mello phanic acid C₆H₂(CO₂H)₄, and prehnomalic acid C₁₀H₈O₆

Salts -The alkaline salts are gummy, v e sol water—The calcium salt is more soluble in hot than in cold water—Pb_A^i (dried at Amorphous pp --- AgaAv1 150°) amorphous

Isohexahydride CoH6(CO2H). Isohydromellitic acid Formed by heating the preceding hexahydride with conc HClAq for 3 hours at 180° (Baeyer) Prisms (from water) V sol water, but ppd on addition of HCl Not affected by heating with fuming HClAq at 300° De composed in the same manner as its isomeride when heated with HSO. Chromic acid mixture oxidises it to acetic acid and CO. -Pb,A'

Methyl ether of the Isohexahydride $\mathbf{M}e_{s}\mathbf{C}_{12}\mathbf{H}_{s}\mathbf{O}_{12}$ [125°] Needles, \mathbf{v} e sol alco

References - Hemi mellitic acid, Pyro MELLITIC ACID

TRIMELLITIC ACID C.H.O. 1.6

C₆H₃(CO H), [1 2 4] Benzene tricarboxylic acid Mol w 210 [218°]

Formation -1 Together with isophthalia acid and pyromellitic anhydride by heating the tetrahydride of pyromellitic acid C,H₆(CO₂H)₄ with 5 pts of H₂SO₄ (Baeyer, A Suppl 7, 40)—2 By oxidising the acid C₆H₄Me(CO₂H)₂, prepared from ψ cumene, by KMnO, (Krinos, B 10, 1491) -3 By oxidising alizarin carboxylic acid with dilute HNO, (Hammerschlag, B 11, 88) — 4 By oxidising the acid C₈H₃Me(C₄H₂)CO₂H

with dilute nitric acid (S G 1 12) at 240° (Effront, B 17, 2338) -5 By the action of cuprous cyanide upon the diazo compound from amido terephthalic acid, and saponification of the product with aqueous KOH (Ahrens, B 19, 1634) heating mono potassic (\$) sulphophthalate with sodium formate, isophthalic acid

being also formed (Graebe a Rée, Č J 49, 532)

Preparation—100 g pulverised colophony
and 2 litres of nitric acid (1 vol commercial acid to 2 vols water) are introduced into a retort with its beak directed upwards, and the liquid is heated to boiling, whereupon the colophony melts, and is quickly attacked, with copious evolution of red vapours, and converted into an orange yellow viscid mass. After the boiling has been continued for 6 or 8 hours, fresh resin and strong nitric acid are added alternately, till about 1 kg resin has been introduced, the con tents of the retort being kept in constant ebulli tion, this process takes about a fortnight. The resulting wine yellow liquid, which on addition of water should merely show turbidity, and not yield any lumpy precipitate, is then distilled off till the remaining liquid begins to froth, and

this liquid, while still hot, is poured into a ten fold volume of cold water, decanted after twentyfour hours from the varnish like resin which separates, and evaporated to a syrupy consist-The whole then solidifies after a while to a thick crystalline pulp, which may be freed from the syrupy mother-houor by means of an aspi rator and porous earthenware plates, and afterwards boiled with water The extract on cooling deposits isophthalic acid in slender needles, and on further concentration, first a little more of the same acid and then trimellitic acid, which may be purified by solution in alcohol and crystallisation from water 30 g of trimellitic acid may be thus obtained from 50 g of resin (Schreder, A 172, 93)

Properties —Rosettes of small needles, m sol water and ether When heated above its melting point the anhydride distils over, con densing in concentrically arranged groups of needles On fusion with NaOH it gives benzene and diphenyl (Barth a Schreder, B 12, 1257) It also yields benzene when distilled with lime

Salts $-Ba_3A'''_2$ 4aq (when air dried) Gives off 3aq at 160° Sl sol water $-Ba_3A'''_2$ 3aq (when dried over H_2SO_4) $-Ag_3A'''$ white pp, not much affected by light sl sol water

Anhydride C₈H₃(CO₂H) CO O [158°] Formed by heating the acid (Baeyer, A 166, 340) Crystalline mass, sl sol cold, v sol hot, water

Reference — Sulpho trimellitic acid
MELLITYL ALCOHOL v Penta methyl
BENZYL ALCOHOL

MELLOGEN C₁₁H₂O₂ On the electrolysis of water by a battery of 1,200 Daniell's cells, the anode being gas carbon, the liquid becomes of an inky colour, and there is deposited in the voltameter a black residue This is washed with water until the filtrate is quite colourless, from the washings the mellogen is ppd with a small quantity of dilute hydrochloric acid (Bartoli a Papasogli, G 11, 468, 12, 117, 13, 37, 15, 464, C R 94, 1339, A Ch [6] 7, 364) A black solid, of conchoidal fracture, sol water and al kalıs, ınsol alcohols and hydrocarbon, and in most mineral acids and salts It is not readily combustible, and is converted by oxidising agents, eg NaOCl, into mellitic and pyromellitic acid and their hydrides At ordinary temperatures it has the composition $2C_{11}H_2O_4 + 3H_2O_7$, at 100° it may be represented by $2C_{11}H_2O_4H_2O$ aqueous solution of mellogen is dark coloured, and is ppd by acids and by many salts baryta mellogen gives an insoluble pp acid (8 G 1 36) oxidises mellogen forming an amorphous compound C₁₁H₂O₂, sol water, alcohol, and ether a soluble acid C₁₁H₂O₂ 2 aq, forming the salts $Ba_3(C_{11}H_3O_7)_2$ and $Ag_3C_{11}\hat{H}_3\hat{O}_7$, and a black compound resembling mellogen.

MELLONE v CYANIC ACIDS
MELLOPHANIC ACID C10H6O8 1 e

C₆H₂(CO₂H), [1 2 3 5] Bensene 1-tetra carboxylic acid [238²] Obtained, together with prehnitio acid C₆H₂(CO₂H), [1 2 3 4], by heating the hydride of pyromellitic acid C₆H₂(CO₂H), [1 2 4 5] with H₂SO₂ (Baeyer, A 166, 327) Formed also by the oxidation of iso-durene C₆H₂Me₄ (Jacobson, B 17, 2516). Small four-sided prisms, v. sol water, but ppd by HCl from a conc. solu-

tion Converted into an anhydride on fusion Calcium acetate gives in hot solutions of the acid a pp which re-dissolves on cooling Baryta-water gives a pp which becomes crystalline on heating Lead acetate gives a floculent pp, insol acetic acid Sodium amalgam forms a hydride of mellophanic acid

Anhydride [238°] Formed by fusing the

cid Insol ether

MELOLONTHIN $C_3H_{12}N_2SO_3$ Found, toge ther with leucine and hypoxanthine, in cockchafers (*Melolontha vulgaris*) The insects are extracted with water, the extract boiled, ppd with lead subacetate, and the filtrate freed from lead by H_sS and evaporated The crystals are freed from leucine by treatment with alcohol (Schreiner, B 4, 763) 30lbs of cockchafers yield 15 g melolonthin Silky needles (from water), sl sol cold, m sol hot, water, v sl sol dilute alcohol and ether, v sol acids and alkalis Does not act on light

MELMESIDINE v DI MESITYL GUANIDINE MENAPHTHYLAMINE $C_{11}H_{11}N$ 2 e

C₁₀H, CH₂NH₂. (292°) Formed by treating the amide of (a)-thionaphthoic acid C₁₀H, CS NH₂ with zinc and HCl (Hofmann, B 1, 100) Alkaline liquid, readily absorbing CO, from the air—B'HCl long, sparingly soluble crystals—

B',H2PtCl, yellow crystalline pp

MENISPERMINE C₁₈H_{.4}N₂O₂ (?) [120°] Occurs in the seeds of Menispermum cocculus (Pelletier a Caventou, A Ch [2] 54, 178) extract the menispermine, the alcoholic extract of the seeds is first treated with cold water, then exhausted with hot acidulated water, the brown solution is ppd by an alkali, and the pp is ex hausted with very weak acetic acid, which leaves a brown black mass undissolved Or the seeds may be made up into a heap, and exhausted with alcohol of specific gravity 0 833, the alcohol distilled off, the residue boiled with water, and the liquid filtered at the boiling heat, it then, on cooling, deposits crystals of picrotoxine, especially if a small quantity of acid has been added. The part insol boiling water is then treated with acidulated water, and ppd by an alkalı, a granular pp is thereby formed, from which alcohol extracts a peculiar yellow sub stance, and the residue is finally dissolved in ether, which deposits menispermine in the crystalline form The ether leaves undissolved a viscous substance, which may be dissolved in absolute alcohol and the solution, evaporated at 45°, ultimately yields crystals of parame nispermine

Properties — Prisms, insol water, sol alcohol and ether Is not poisonous Its sulphate

forms prismatic needles, sol water

Paramenispermine [250°] Isomeric with menispermine Insol water, sl sol ether, v sol boiling alcohol Dissolves in dilute acids

sol boiling alcohol Dissolves in dilute acids MENTHENE C₁.H.₁ Mol w 138 (167 4° cor) (Atkinson a Yoshida, C J 41, 53), (163°) (Oppenheim, C J 15, 29) V D 4 94 (calc 4 78) S G 15 814, 2 8226, 20 8073 (A a Y) C E (0°-10°) 000994, (0°-60°) 00100 [a]₃ = +13 25 (A a Y) R₁₀ 74 0 Specific refractive energy, 548 Specific dispersive energy, 0313 (Glad stone, C J 49, 622) Obtained by distilling menthol (1 pt) with ZnCl₂ (2 pts), or with P₂O₃ (Walter, A. 32, 288) Formed also by the action

of cone H,SO, on menthol (Beckmann, 4 250,

Properties — Colourless oil, smelling like cymene, m sol ether and alcohol, v sol benz ene, turpentine, and petroleum Dextrorota torv

Reactrons —1 Combines with fuming HCl, forming a yellow oil $C_{10}H_{10}Cl$ Combines also with HI, forming $C_{10}H_{10}I$, identical with the product obtained by heating terpliene dihydro disolde $C_{10}H_{16}2Hl$ with HI (Bouchardat a Lafont, C R 107, 916) —2 Combines with bromine, forming $C_{10}H_{18}Br_4$, which is split up by heat into HBr and cymene (Beckett a Wright, C J 29, 1) 8 Fuming natric acid oxidises it to glutaric acid

8 Fuming nutric acid oxidises it to glutaric acid

MENTHOL C₁₀H₂₀O i e

C₃H, CH<

CH₂—CH₂

CH₂ CH CH₃

CH CH₄

CH CH₂

CH CH₂

CH CH₃

CH CH₄

CH CH₄

CH CH₄

CH CH₅

CH CH₅

CH CH₄

CH CH₅

 C_2H , $CH < \frac{CH_2}{CH_2} \frac{CH_2}{CH(OH)} > CH CH_3$ (?) Methylpropyl phenol herahydride Mol w 156 (212°) VD 562 (calc 541) SG SG 15 890 596 (Oppen [a]_j = -59 3 (Morrya), [a]_b = -59 6 (Oppen heim), = -49 4 in a 5 p c alcoholic solution at 22° (Arth, A Ch [6] 7, 438) $R_{\infty} = 77.4$ in a 21 pc benzene solution (Kanonnikoff, J pr [2] 31,348) HC 1,509,100 (Louguinine, A Ch [5] 23, 387) Deposited in crystals when the essential oil of peppermint is kept for a long time or cooled to a low temperature (Dumas, A 6, 252, Blanchet a Sell, A 6, 293, Walter, A 32, 288, Kane, P M 16, 418, Laurent, Rev Scient 14, 341, Oppenheim, C J 15, 24) Menthol is imported from Japan in the solid state as 'peppermint camphor' (Moriya, C J 39, White crystals, smelling of peppermint, il sol water, ve sol alcohol, ether, CS2, HOAc, and fixed and volatile oils Insol aqueous al and fixed and volatile oils kalıs From alcoholic NaOH it crystallises in long needles Sodium dissolves in it with evolu tion of hydrogen Cone acids dissolve menthol, but it is reppd on dilution with water Menthol has the refractive and dispersive energy of a saturated compound (Gladstone, C J 49, 621) The rate of etherification of menthol by acetic acid is that of a secondary alcohol (Menschut kin, J R 13, 569)

Reactions—1 With K₂Cr₂O, and H₂SO₄ in seal.d tubes at 120° gives an inactive oil 'men thone' (205°), C₁₀H₁₈O, S G 15 9032, sol alco hol, ether, and chloroform—2 Fuming HNO, brms an explosive oil, S G 15 1061, which may be reduced to a yellow oil C₁₀H₁₈NH₂(185°-190°) 3 Excess of fuming HNO, forms an acid, probably glutario (q v)—4 Bromine in acetic acid forms C₁₀H₁₈Br Unstable oil—5 Cone HClAq at 100° slowly forms menthyl chloride PCl₃ forms the same body—6 ZnCl₂ or P₂O₃ dehy drate menthol, producing menthene—7 KMnO₄ in acid solution forms (β) pimelic acid C,H₁₀O₄ [87°], of which the amide [191°] crystallises from water in prisms (Arth, A Ch [6] 7, 440, C R 107, 107) Formic, propionic, butyric, and oxymenthylic acids are formed at the same time The oxymenthylic acid C₁₀H₁₈O₄ boils at 174° under 15 mm pressure—8 Boiled with HI (S G 17) for 3 days it forms a mixture of hydrocarbons chiefly consisting of C₁₀H₁₈ (168 6°) V D 67 25, [a]₂=+52 S G 2 8254, 28 111, C E (0°-10°) 000929, (0°-60°) 000694 R₂₀

benzene, less so in alcohol or ether Odour resembles symene (Aktanson a Yoshida, C J 41, 54) —9 Menthol does not react with hydroxylamine (Nageli, B. 16, 499) —10 On heating with sodium and ether on the water bath, and, after cooling, adding CS₂ there is formed menthyl-xanthogenic acid $C_{10}H_{20}$ CS SH, a liquid which undergoes spontaneous decomposition, but forms a yellow crystalline copper salt CuA'_{2} (Bamberger a Lodter, B 23, 213)

Acetyl derivative $C_{10}H_{19}OAc$ Menthyl acetate (223°) [a] = -114° From menthol and HOAc at 120° (Oppenheim, C J 15, 26) Liquid Not decomposed by cold alkalis, but saponfied by alcoholic NaOH at 120°

Butyryl derivative C₁₀H₁₀O CO C₃H₇.

Menthyl butyrate Obtained by heating menthol with butyric acid at 200° for 30 hours (Oppen heim) (230°-240°) [a] = -89°

Benzoy l derivative $C_{10}H_{10}OBz$ [54°] (230°) [a]₀ = -91° In a one p \bar{o} benzene solution, trimetric crystals putially decomposed on distillation into menthene and benzoic acid (Arth, A Ch [6] 7, 479)

Carbamyl derivative $C_{11}H_{21}NO_{2}$ s.e $C_{12}H_{12}OCONH_{2}$ Menthyl carbamate [165°] $[165^{\circ}]$ and 58 pc chloroform solution at 21° Formed by passing dry cyanogen into a solution of sodium menthol in dry toluene. The product is washed with water and the toluene distilled off. The crystalline mass is then recrystallised from alcohol, from which the carbamyl derivative separates in slender prismatic needles (Arth, CR 94, 872, 98, 521, ACh [6] 7, 433) Needles, m sol alcohol and benzene Subhmes at 100° Decomposes at about 200°, yielding cyanuric acid Alcoholic KOH forms menthol and potassium cyanate $Ac_{2}O$ at 130° forms $C_{2}H_{10}OAC$ Benzoic aldehyde and HCl form $(CH_{10}CONH)$ CHP1 [142°]

and HCl form $(C_{10}H_{10}OCO NH_2CHPh [143°] Carbonyl derivative <math>(C_{10}H_{10}O)_2CO Menthyl carbonate [105°] Obtained in the preparation of the carbamyl derivative by eva porating the alcoholic mother liquor and boiling the residue with water as long as menthol and ammonia come off On cooling, the carbonyl derivative is deposited as a crystalline mass, sol boiling alcohol (Arth) Plates (from alcohol) or prisms (from toluene), v sl sol alcohol, v sol ether and benzene Alcoholic KOH at <math>100^\circ$ saponites it

Phenyl-carbamyl derivative
C₁₀H₁₀O CO NHPh Menthyl phenyl urethane
Menthyl phenyl carbamate [111°] From men
thol and phenyl cyanate (Leuckart, B 20, 115)
Silky needles (from hot alcohol)

Succinoxyl derivative $C_{10}H_{10}O$ CO CH_2 CH_2 CO, H [62°] [a]_D = -59 6° in a 1 4 pc benzene solution Formed by heating menthene (1 mol) with succinic anhydride (1 mol) at 110° (Arth) Acicular crystals, vesol alcohol, velecity solutions and K salts are very deliquescent, the Ca and Basalts are white pps $-AgC_{14}H_{22}O_4$ small needles (from hot water)

Succinyl derivative $(C_{10}H_{10})_2C_4H_4O_4$. [62°] (220°) $[a]_D - 81$ 5° in a 1 9 p c benzene so'ution From menthol (1 mol) and succinic acid (2 mols) at 150° Trimetric crystals (from alcohol) Decomposes on distillation into succinic acid and menthene.

204 MENTHOL

Phthaloxyl derivative C18H2,O4 re $C_{10}H_{10} O CO C_6H_4 CO_2H [110°] [a]_D = -105 6°$ in a 16 pc benzene solution Formed by heating menthol (1 mol) with phthalic anhydride (1 mol) at 110° (Arth) Minute needles, insol cold water, y sol alcohol and ether Gives white pps with Ba and Ca salts -Mg(C18H23O4) lamine, almost insol cold water

Phthalyl derivative $C_{28}H_{42}O_4$ s.e $(C_{10}H_{19})_2C_8H_4O_2$ [133°] $[a]_D=-94$ 7° in a 2 pc benzene solution at 20° From phthalic anhydride (1 mol) and menthene (2 mols) at 140° Trimetric crystals (from ether), sl sol

boiling alcohol

Menthyl chlorade C10H19Cl (c 204°) Ob tained by treating menthol with PCl, (Walter, A 82, 292) or with cone HClAq for a week at 100° (Oppenheim) The same body appears to be formed by heating menthene with fuming HClAq at 120° (Arth, C R 97, 323) Light oil, sl sol water, m sol alcohol Not attacked by alcoholic KOH With sodium menthol it gives menthene and menthol

Menthyl bromide C10H19Br From menthol and bromide of phosphorus Non volatile liquid

Gives with bromine $C_{10}H_{14}Br_6$ Menthyl iodide $C_{10}H_{19}I$ From menthol and conc HIAq Liquid, decomposed by alcoholic

K2S into menthene and HI

Tetra menthyl silicate Si(OC10H19)4 (350°) at 155 mm Formed by the action of SiCl, upon menthol, the yield is 75 pc of the theo retical (Hertkorn, B 18, 1695) Colourless prisms, v sol ether, benzene, ligroin, chloroform,

CS₂, and warm alcohol, sl sol cold alcohol
Oxymenthylic acid C₁₀H₁₈O₃ (175°) at 15 mm (280°) A product of the oxidation of menthol by KMnO, (Arth, A Ch [6] 7, 448) Colourless liquid, partially decomposed on boiling at 280°, v sl sol water, v sol alcohol and ether salts of alkalis and alkaline earths are very soluble A solution of the sodium salt is ppd by salts of Pb, Fe", Cu, and Pt It forms no white deli acetyl derivative -AgA' -NaA' quescent crystals

Methyl ether MeA' (137°) at 17 mm

Liquid

Ethyl ether EtA' (145°) at 18 mm

Thick liquid

MENTHONE $C_{10}H_{18}O$ (206 3° cor) [a]₁ = +21° S G $\frac{9}{2}$ 9126, $\frac{49}{12}$ 8972 C E (0°-10°) 000862, (0°-100°) 000923 R $_{\infty}$ 75 3 From menthol (30 g), K₂Cr₂O₇ (10 g), and H₂SO₄ (10 g) at 155° The light oil is subjected several times to the action of the same oxidising mixture (Atkinson a Yoshida, C J 41, 49) Colourless oil, miscible with alcohol, chloroform, benzene, and CS₂ Smells like diluted peppermint Does not combine with NaHSO₃ If a solution in petroleum is treated with Na and CO₂ successively and then shaken with water crystals of menthol are got [42°], but having [a]_j = -39° not -59° Levo-menthone C₁₀H₁₈O : e

 $CHPr < \begin{array}{c} CH_2 \\ CH_2 \\ CO \end{array} > CHMe (?) \quad (207^\circ)$ S.G -8960 $[a]_D = -282^\circ$ Menthone is a mixture of two isomerides-one dextro, the other lævorotatory By using very little acid the lævomenthone may be obtained free from dextromenthone and menthol The best proportions are 60 g. K₂Cr₂O₂, 50 g H₂SO₄, 300 g water, and

45g menthol, the mixture being kept at 30° to 55° (Beckmann, A 250, 325) The menthone is extracted with ether, washed with dilute alkalis, and distilled with steam

Properties - Mobile liquid, smelling faintly of peppermint, sl sol water, miscible with al of peppermint, s. sor warre, cohol, ether, and petroleum ether. The mole cular weight determined by Raoult's method carees with the formula. The molecular re

fraction $\left(\frac{n^2-1}{n^2+2}\right)^{\text{P}}_{\vec{d}}$ is 46.3 Leevo menthone is

converted into a mixture of dextro and lævo menthone by acids, bases, water, heat, or even on keeping

Oxim C_1 H_{18} NOH $[a]_D = -42.5^{\circ}$ Crystall Mol w 169 Crystalline, sol dilute alcohol, ether, and petroleum ether Raoult's method gives, when acetic acid is used, the mol w 169, but when benzene is used it gives 251 With HCl the oxim forms a compound (C₁₀C₁₈NOH)HCl [119°], a white orystalline

powder - × C₁₀H₁₈NONa

Dextro menthone $C_{10}H_{18}O$ Mol w 154 (208°) SG $\frac{20}{20}$ 900 [a]_p = +28 14° Obtained by freezing a mixture of H SO₄ (10 pts) and water (1 pt), adding menthene, (2 pts), and shaking The temperature is slowly raised to 30°, the product poured into ice, and the men-thone extracted by ether (Beckmann, A 250, 334) Colourless mobile oil, sl sol water, miscible with alcohol, ether, and petroleum ether The mol w determined by Raoult's method is 150 The action of acids, bases, water, heat, and time convert dextro menthons into a mixture of dextro and levo menthone Oxim C₁₀H₁₈NOH Thick oil, slightly levo

rotatory The mol w determined by Raoult's method is 165 when acetic acid is used, and 228 when benzene is employed as solvent — (C₁₀H₁₈NOH)HCl [6 97°] Deliquescent —

*C₁₀H₁₈NONa

MENYANTHIN C₉₀H₄₆O₁₄ [60°-115°] A bitter glucoside found in buckbean (menyanthes trifoliata) (Brandes, Kromayer, Ar Ph [2] 108, 257, 124, 37, Fr 1, 15) Prepared by treating the aqueous extract with animal charcoal at 65°, and subsequently extracting the charcoal with alcohol Amorphous yellowish mass, sl sol cold water, v sol hot water and alcohol, insol ether Dissolves in aqueous alkalis Its solutions are not ppd by metallic salts It is ppd by tannin When distilled with dilute H₂SO₄ it gives off volatile menyanthol, while glucose C₆H_{1,O₆} Gaq remains behind

Menyanthol C₈H₄O is an oil smelling like benzoic aldehyde

It reduces ammoniacal

benzoic aldehyde It reduces ammoniacal AgNO₈ By exposure to the air, or by potashfusion, it is converted into a crystalline sub-

limable acid

This name has also been Menyanthin applied to inulin when prepared from buckbean

MERCAPTALS Compounds of the form RCH(SR')2 They may be viewed as thio acetals or as the sulphur compounds corresponding to the alkyl derivatives of ortho aldehydes THIO ALDEHYDES

 MERCAPTAN
 C₂H₂S t.e
 C₂H₄SH
 Ethyl

 mercaptan
 Thro alcohol
 Mol w 62
 (36 5°)

 S G ³⁰
 8391
 V D 211 (calc 2 15)
 S V 76
 (Lousen, A. 264, 71) H.Fp. 14,480. HF.v. 18,271 (Thomsen) R_{∞} 18 62 (Nasını, G 18,

Formation —1 By distilling calcium ethyl sulphate (Zeise, P 31, 369) —2 A mixture of alcohol and H₂SO₄ is neutralised with KOH, decanted from ppd K₂SO₆, mixed with excess of KOH, saturated with H₂S, and distilled (Wohler) —3 A solution of KOH (S G 13) is saturated with H₂S, mixed with an equal volume of a cone solution of KEtSO₄, and distilled from a water bath (Liebig, A 11, 14, 23, 34) The product is freed from Et₂S by fractional distillation (Claesson, J pr [2] 15, 193) —4 From KSH and EtCl (Regnault, A Ch [2] 71, 390) —5 From KSH and LtI (Baudrimont, C R 54, 616) —6 By reducing with HI a'·160° the solid thio aldehyde obtained by passing H₂S into a mixture of aldehyde solution and iodine (Bot tinger, B 11, 2203) —7 Together with HEtSO₄ and ether, by heating alcohol saturated with SO₂ in sealed tubes (Endemann, A 140, 336, Pagliam, B 11, 155)

Preparation —A cold mixture of alcohol (1 litre) and H₂SO₄ (500 c c) is diluted with ice and then added to a solution of crystallised so dium carbonate (4 kilos) —The product is concentrated until Na₂SO₄ separates —The mother liquor is further concentrated, and mixed with KOH (800 g) dissolved in water (1,500 c c) previously saturated with H S. The whole is heated on a water bath, and the gases are passed first through a strong solution of caustic potash (50 g) and then into a solution of KOH (350 g) in water (700 g) —The small amount of H₂S contained in the latter solution is ppd by lead acetate, and the mercaptan liberated by HCl. It is dried with K₂CO₃ and distilled (Klason, B 20, 3407)

Properties - Colourless, very mobile, liquid, having a peculiarly persistent alliaceous odour V sl sol water, miscible with alcohol and ether Very inflammable, and burns with a blue flame A drop of it when briskly agitated on the end of a glass rod becomes solid, possibly through formation of a hydrate Neutral to litmus alcoholic solution forms a yellow pp with lead salts, and white pps with cupric acctate, mer curic salts, and trichloride of gold. The alco holic solution is turned blue by FeCl, (Rathke, A 161,148) Mercaptan is a reducing agent thus it converts nitro benzene into azo benzene Mer captan decomposes salts of phenyl with forma tion of sodium phenylate and a thio ether (R Seiffert, J pr [2] 31, 462) But with phenyl salicylate it acts thus C,H4(OH)CO,Ph+NaSEt = C_sH₄(ONa)CO₂Ph + HSEt A trace of isatin dissolved in sulphuric acid gives, with a trace of mercaptan, a fine green colouration (Berthelot, C R 108, 350)

Reactions—1 Boiling netric acid (S G 14) becomes red, deposits an oil, and ultimately forms ethane sulphonic acid Weaker nitric acid (S G 128) forms EtsO₂SEt.—2 Potassium forms hydrogen and KSEt—8 P₂S₅ forms Et₂PS₄ and Et₂HPS₄ (Carius, A 112, 190)—4 Bromme forms EtBr and S₂Br₂ (Friedel a Ladenburg, A 145, 189)—5 Heated in sealed tubes with diaso-compounds (diazo salicylic acid diazo phenol chloride) it forms di ethyl disulphide, the diaso-compound being reduced exactly as when

boiled with alcohol (R. Schmitt a O. Mittenzwey, J. pr. 126, 192). C₂H₄(OH) N NCl + 2EtSH = Et₁S₂ + N₂ + C₆H₅ OH + HCl — 6. PCl₅ at 100° forms thiophosphorous ether P(SEt)₃, a fetid oil, resolved by distillation into phosphorus and Et₂S₂ — 7. CCl₄, acting on NaSEt, forms C(SEt)₄ a light oil, S. G. 1.01, decomposed on distillation C. Cl₅ with NaSEt gives C₂(SEt)₆, a heavy fetid oil, solidiying at very low temperatures. C₂Cl₄ heated with NaSEt at 100° gives C₂(SEt)₄, crystallising in rhombohedra [54°] — 8. S.Cl₂ forms HCl and Et₂S₄, which is resolved by distillation into Et₂S₂ and S₂ — 9. TCl₄ gives EtSHTiCl₄ and (EtSH)₂TiCl₄ (Demarcay, Bl. [2] 20, 132) — 10. Reacts with ketones forming 'mercaptoles' or thioketates. Thus HCl passed into a mixture of acetone and mercaptan forms (CH₃)₂C(SEt)₂ (Baumann, B. 18, 887) — 11. Mercaptan sus pended in ice water and mixed with diazobenzene sulphonic acid and soda gives explosive yellow needles of SO₂Na C₂H₄, N, SEt. When the alcoholic solution of this salt is boiled SO₂Na C₂H₅, SFt and nitrogen are formed (Stad ler, B. 17, 2075)

Salts — All metallic mercaptides are decom posed by HCl -- KSEt From mercaptan and Dull white granular mass, v sol water, sl sol alcohol Its aqueous solution gives a yellow pp with lead salts - NaSEt From mercaptan and Na or NaOEt Crystalline mass, v sol water and alcohol Its aqueous solution is alkaline in reaction, and gives off all its mercap-tan on boiling. In dry air it oxidises to C2HSO3Na When oxygen is passed through its alcoholic solution Et.S is formed -Zn(SEt)2 white, indistinctly crystalline pp obtained by adding mercaptan to aqueous zinc acetate NH, Aq and reppd on neutralisation - Cd(SEt), -Co(SLt), gummy pp Unlike the other mercaptides it is not attacked by fuming HNO, --Ni(SEt), chocolate brown powder, not decomposed by water—*Fe(SEt), from FeCl, mercaptan, and ammonia Black slimy mass, re solved by heating into mercaptan and ferrous hydrate —LtSFe(NO), [78°] From KSFe(NO), and EtI (Pavel, B 15, 2607)—TISEt yellow curdy pp, sl sol water -Cu(SEt)2 Obtained by adding mercaptan to a solution of CuSO. mixed with NaOAc Pale yellow amorphous powder (klason, B 20, 3407) —Hg(SEt), [77°] S 7 in 85 p c alcohol Formed on shaking HgO with mercaptan or with an alcoholic solution of mercaptan, the action being attended with great evolution of heat It is from this body that mercaptan derives its name (corpus mercurio aptum) White unctuous scales When its alcoholic solution is heated to 190° it is decom posed into mercury and Et S, (Otto, B 13, 1289, 15, 125) The same decomposition appears to occur when it is heated in the dry state. It is not decomposed by aqueous KOH, but aqueous K2S forms some HgS and KSEt H.S forms HgS and mercaptan Nitric acid oxidises it to (C₂H₃SO₃)₂HgHgO When melted with lead the products are mercury, PbS, and Et2S Mercury mercaptide forms with iodoform needles of ((EtS) Hg), CHI, [85 5°] (Jackson a Oppenheim, B 8, 1033)—EtSHgCl White bulky pp obtained on mixing an alcoholic solution of mercaptan with HgČl₂ Changes after some time to crystalline laminæ Sl. sol. water and ether, m sol boiling alcohol (Debus, A 72, 18) -Pb(SEt)₂ Yellow pp, got by mixing alcoholic solutions of lead acetate and mercaptan composed by heating with alcohol at 190° into PbS and Et₂S —B₁(SEt)₂ [79°] Obtained by mixing a solution of a salt of bismuth with mer-Long flexible yellow needles, m sol alcohol and ether Oxidises in the air Resolved by heat into BiS and Et,S -Sn(SEt). Formed by mixing solutions of mercaptan and SnCl, in Also from CS₂, and evaporating the solvent mercaptan and a conc aqueous solution of Oil, remaining liquid at -40° May be distilled in vacuo, but when heated under atmospheric pressure it decomposes yielding Et.S. and metallic tin -Sn(SEt), yellow pp which quickly oxidises in air -EtSSbCl2 formed by evaporating a mixture of mercaptan and SbCl. Decomposed by water with libera tion of mercaptan -As(SEt)3 Obtained by adding NaSEt to an ethereal solution of AsCl. Oil, with unpleasant odour Decomposed on distillation into arsenic and Et₂S. —ClAs(SEt), From AsCl, and mercaptan in the cold —EtSAu White gelatinous pp obtained on mixing dilute alcoholic solutions of auric chloride and mercaptan -Pt(SEt), light yellow pp -Rh2(SEt), yellow pp

Hydrate EtSH 18H2O Solidifies as a crys talline mass when moist vapour of mercaptan is passed through a condenser cooled below 8° (H Muller, Ar Ph [2] 150, 147) Mass of small needles, insol water and mercaptan pound containing 16 p c carbon, crystallising in prisms, is obtained by pouring mercaptan into a solution of H₂S at 0° It perhaps contains

 ${
m H_2S}$ as well as water It melts and decomposes above 3° (Blankie, Pr E 10, 87) **MERCAPTANS** (Sulphydrates) Compounds of the formula RSH where R is a hydrocarbon radicle They may be viewed as acid ethers of sulphydric acid or as alcohols in which O has been displaced by S Just as H₂S is more acid than H₂O, the mercaptans are more acid than the alcohols Thus they readily form salts by reacting with metallic oxides, and they derive their name from the ease with which they form mercuric salts The salts of mercaptans may be called mercaptides The mercaptans boil at a lower temperature than the corresponding alcohols, just as H2S has a lower boiling point than H_0 The mercaptans have an unpleasant odour. They are very readily oxidised, forming disulphides R_2S_2 , and finally sulphonic acids The oxidation to sulphonic acids is best effected by nitric acid, and the chlorides of the sulphonic acids RSO2Cl when reduced by tin and HCl yield the mercaptans again (Vogt, A 119, 152) By heating mercaptans with H₂SO₄ disulphides R₂S₂ are formed (Erlenmeyer

a Lisenko, J 1861, 590)

Preparation—1 Fatty, but not aromatic, mercaptans are formed by heating a solution of KSH with alkyl chlorides or iodides or with potassium alkyl sulphates -2 By heating alco hols or phenols with P_2S_5 (Kekulé, A 90, 311, Z 1867, 193) The yield is small -3 By reducing chlorides of sulphonic soids with zinc or tan and dilute H2SO, or HCl This process is very convenient for the preparation of aromatic mercaptans The product is distilled with steam.

4 Aromatic mercaptans may be prepared by treating diazo compounds with K28 (Klason, B. 20, 350) -5 Aromatic mercaptans may be obtained by reducing the corresponding disulphides with zinc and H2SO, -6 Aromatic mercaptans can be formed, together with the corresponding sulphides, by the action of aluminium chloride on a mixture of hydrocarbon and sulphur at 80° (Friedel a Crafts, Bl [2] 31, 464) -7 When three atoms of hydrogen in the benzene nucleus have been displaced by chlorous radicles, and two of these are NO, and a halogen in ortho position to each other, alcoholic KSH displaces the halogen by SH (Beilstein a Kurbatoff, A 197, 75) -8 By treating aromatic diazo compounds with sodium thiosulphate and reducing the resulting aromatic thiosulphates with zinc and H_2SO_4 (Leuckart, G P 1887, 45,120)

Properties — Oils or crystalline solids with pleasant odour Insol water The salts of unpleasant odour Insol water the heavy metals are sparingly soluble in water The mercuric salts can usually be recrystallised from alcohol When a small quantity of a 1 p c solution of isatin in H2SO4 is mixed with a few c c of the strong acid and a small quantity of a fatty mercaptan, a green colouration is produced Aldehydes and the higher alcohols interfere with the isatin reactions, and in this case the liquid may be shaken with a solution of KOH and then mixed with a little sodium nitro prusside, when a reddish violet colouration is produced (Deniges, C R 108, 350) The alkyl sulphides do not give this reaction sulphides are present they should first be ppd by an alkaline solution of PbO

Reactions -1 The ammoniacal solutions of aromatic mercaptans oxidise in the air with formation of disulphides —2 When HCl is passed into a mixture of a ketone and a mer captan condensation takes place and a thicketate

or 'mercaptole' is formed, eg(CH₃)₂CO + 2HSEt = (CH₃)₂C(SEt)₂ + H₂O
(Baumann, B 18, 887) -3 The alkoyl deriva tives of aromatic o amido mercaptans readily split off H2O, forming anhydro compounds, e g $C_6H_4 < \frac{NH}{SH}COCH_7 = H_2O + C_6H_4 < \frac{N}{S}CCH_8$

These anhydro- compounds may even be formed by boiling the alkoyl derivatives of aromatic amines with sulphur They are also formed by the oxidation (by K,FeCy, of the thio alkoyl They are vola derivatives of aromatic amines tile liquids which exhibit feeble basic characters, and regenerate the amido mercaptans when fused with potash (Hofmann, B 13, 8, 1223, Jacob sen, B 19, 1069) When o amido mercaptans are diazotised they produce characteristic stable compounds of the form $C_6H_4 < N > N$

MERCAPTURIC ACIDS Acids obtained by placing chloro- or bromo benzene in food eaten by dogs V Bromo PHENYL and CHLORO PHENYL-MERCAPTURIO ACIDS

MERCURAMMONIUM COMPOUNDS monro mercury compounds Ammoniacal mercury bases Mercuramines) By the reactions of ammonia, or ammonium salts, on compounds of Hg, compounds are obtained, many of which may be represented by the empirical formulæ xHgX yNH_s and xHgX₂ yNH_s where X = acidic radicle, some of the compounds, however, contain N and H in the ratio N H2, and some are composed of N, Hg, and acidic radicles only The mercurammonium compounds, as a class, do not react as loose compounds of Hg salts with NH, but rather as compounds of Hg, N, H, and acidic radicles

The mercurammonium compounds were regarded by Kane as compounds of NH2Hg Thus, the compound HgO NH, was formulated as NH,Hg OH, and the compound HgSO, 2NH, as NH2Hg O SO,ONH, (A Ch [2] 72, 215) Hirzel (A 84, 258) represented the mercurammonium compounds as compounds of mercuric nitride, N₂Hg₃ Gerhardt suggested that these compounds are derived from NH₃ by replacing H by Hg, and after the ammonium hypothesis had been somewhat developed, Hofmann attempted to derive the compounds in question from different hypothetical mercurammoniums, ve compounds formed by replacing the H of NH, more or less completely by Hg (v Handwörterbuch der Chemic [2nd ed] 2, 751, cf Schmieder, J pr 75, 147, Nessler, J 1856 409) On this view, the compounds HgCl22NH2 and HgSO42NH2

are represented as Hg</r>
NH,Cl and

NH So. The mercurammonium compounds

may be divided, on this view, into classes ac cording to the hypothetical Hg derivative of am monium from which they are supposed to be derived Thus we have the following N2H6Hg = mercurammonium, N.H, Hg2 = mercurosammo nium, $N_2H_1Hg_2 = dimercurammonium$, $N_2H_1Hg_4$ = dimercurosammonium, the mercurammonium compounds are those containing divalent Hg, and the compounds of monovalent Hg are called mercurosammonium derivatives The compound 2HgO NH, obtained by the reaction of HgO with NH, Aq, is represented on the ammonium hypothesis as hydrated mercurammonium hy droxide, NHg,OH H,O

A division is sometimes made between those mercurammonium compounds which contain N and H in the ratio N H, and those which con tain these elements in the ratio N H2, the latter are called mercuramide compounds

Although some compounds readily give off NH, when heated, and others only when heated with alkali, yet it seems simpler to name all the compounds under consideration in accordance with the ammonium hypothesis In this article the mercurammonium compounds are divided into two classes, mercurous and mercuric, the former being called mercuro and the latter mercuri compounds, the name given to each com pound is intended to indicate the number of NH, groups from which the compound is derived, and the number of Hg atoms (mercuro- or mercuri) in the formula Several compounds are known whose reactions beem well expressed by supposing them to contain the group Hg O Hg, such compounds are called mercur oxy ammonium derivatives in this article

The following table presents the classifica tion and nomenclature adopted in the present article --

MERCUROUS COMPOUNDS

Series (1) Mercuro - ammonium com pounds , eg (NH,Hg)Cl.

(11) Dimercuro-ammonium compounds, eg (NH,Hg,)Cl

Class II MERCURIC COMPOUNDS

> Series (1) Mercuri - ammonium pounds, e g (NH₂Hg)Cl

(11) Dimercuri-ammonium compounds, eg (NHg₂)₂O

(111) Mercuri diammonium com pounds, eg (N_iH_iHg) I_i

(1V) Dimercuri - diammonium

compounds, eg
(N,H,Hg,)SO, HO
(v) Trimercuri - diammonium
compounds, eg $(N_2H_2Hg_3)SO_42H_2O$

Class III MERCUROXY AMMONIUM COMPOUNDE, e g (NH Hg₂O)OH, (NH₂Hg₂O)₂SO₄ Dimercuro ammonium chloride (NH₂Hg₂)Cl

18 sometimes called mercuro chloramide or amido mercurous chloride, to express this view of its constitution the formula is written Hg (NH₂)Cl So also mercuro ammonium chloride (NH, Hg)Cl is sometimes called ammo nio mercurous chloride, and the formula is written, empirically, HgCl NH₃, the for mula of this compound is frequently doubled, and the name mercurosammonium chloride-(N2H6Hg2)Cl2-18 given to it The salts called in this article mercuroxy ammonium compounds may be regarded as hydrated dimercuri ammo nsum salts, thus, the chloride (NH₂Hg₂O)Cl may be written (NHg)Cl H.O, and the car be bonate (NH2Hg.O)2CO3 may (NHg)2CO, 2H2O

Class I MERCUROUS COMPOUNDS NH,-xHgxX. The experiments of Barfoed (J pr [2] 39. 201) make it probable that the so called mer curo ammonium compounds are really mixtures of mercuri compounds and Hg B asserts that exactly half the Hg in the black pps formed by NH,Aq in solutions of mercurous salts exists uncombined, that nearly the whole of this Hg disappears as vapour when the pps are freely exposed to air, and that the light coloured com pounds remaining are the same as those pro duced by adding NH, Aq to mercuric salts the pp produced from HgNO, Barfoed gives the composition 3Hg + 2(HgNH, NO₃)HgO, that produced from Hg₂SO₄ is 4Hg + (NH₂Hg)₂SO₄ 2HgO, that from HgCl is Hg + NH₂HgCl, and that from Hg C₂O₄ is 4Hg + (NH₂Hg)₂C₂O₄ 2HgO

Series (1) Mercuro ammonium compounds: NH.HgX

Mercuro-ammonium chloride, (NH,Hg)Cl. (Ammonio mercurous chloride (HgCl NHs) Mer curos ammonium chloride (N2H6Hg2 Cl2)) black powder, obtained by saturating HgCl, pre pared by ppn, with NH, gas, on gently warming all NH, is given off (H. Rose, P. 20, 158) The dissociation of this compound has been studied by Isambert (C R 66, 1259, v Dissociation, vol ii p 397) According to Barfoed (J pr [2] 39, 201) the compound formulated as above is really a mixture of Hg, mercuri-ammonium chloride (NH2HgCl), and NH4Cl.

Series (11) Dimercuro-ammonium com-pounds, NH₂Hg₂X

Dimercuro ammonium chloride, (NH2Hg2)Cl (Mercurochloramide or amido-mercurous chloride (Hg,NH, Cl) Tetramercuro - diammonium chloride (N,H,Hg, Cl₂)) A black solid, obtained by digesting HgCl with NH,Aq (2HgCl + 2NH,Aq = NH,Hg₂Cl + NH,ClAq) Becomes dark grey when dried, heated, gives off NH, and N, and at a higher temperature yields a sublimate of HgCl and Hg, treated with HCl gas, gives HgCl and NH,Cl (Kane, A Ch [2] 72, 215, Ullgren, P 42, 395) According to Barfoed (J pr [2] 39, 201) the black solid obtained as described is a mixture of Hg and NH2HgCl

Mercuro ammonium nitrates Various com pounds of the form xHg₂O yN₂O₃ zNH₃ have been described by Kane (lc) and Mitscherlich (P9,387, 16, 41), but Barfoed's experiments make it very probable that these bodies are mixtures of Hg and mercuri ammonium salts (v supra)

Class II. MERCURIC COMPOUNDS N.H. H. W. Hgy X.

Series (1) Mercuri ammonium compounds, NH₂HgX Obtained by interaction of excess of NHaAq with mercuric salts in solution

Mercuri-ammonium chloride, (NH2Hg)Cl (Mercuri-chloramide, or amido mercuric chloride (Hg NH₂ Cl) Dimercuri diammonium chloride (N₂H₄Hg₂ Cl₂) Infusible white precipitate) Ac cording to Rammelsberg (J pr [2] 38, 558) this salt is a double compound of dimercuri ammo nium chloride-NHg,Cl-and NH,Cl, R assigns to it the formula NHg₂Cl NH₄Cl (v infra)

When excess of NH3Aq is added to HgCl2Aq, or when HgCl2Aq is dropped into NH3Aq, a white pp is obtained, this pp was long considered identical with that obtained by adding Na, CO, Aq to HgCl₂Aq mixed with NH₄ClAq, and known in pharmacy as Mercurius precipitatus albus Wohler (P 26, 203) found that the pp formed by NH3Aq was volatilised without fusion when heated in a Pt dish, but that the pp formed by Na₂CO₃Aq melted before it volatilised by NH, Aq was then called infusible white precipitate, and to that produced by Na, CO, Aq the

name fusible white precipitate was given
Preparation —HgCl₂Aq is added to excess of cold NH, Aq, the pp is collected at once, rapidly washed with a little cold water, and dried at 110° (André, C R 108, 233, 290) André (lc) has examined the compounds obtained by the interaction of NH, Aq with HgCl2Aq, varying the relative masses of the reacting bodies and the time of contact Using equal volumes of HgCl2Aq, containing 33 875 g HgCl₂ per litre, and NH₂Aq containing 4 25 g NH₃ per litre, the pp after drying at 110° was not quite pure NH₂HgCl, but contained a little mercuroxy ammonium chloride (NH₂ Hg₂O)Cl The quantity of (NH₂ Hg₂O)Cl increased by allowing the reacting bodies to remain in contact, and also by increasing the quantity of NH, Aq, when the NH, and HgCl2 were present in the ratio 6NH, HgCl2, the pp contained equal molecular proportions of NH2HgCl and (NH₂ Hg₂O)Cl, and by further increasing the NH₃, only (NH₂ Hg₂O)Cl was obtained André found that NH₄Cl tends to change (NH₂ Hg₂O)Cl into NH. HgCl, by adding 1 vol HgCl, Aq to 5 vols NH, Aq (strength as given above), decanting after 24 hours, and agitating the pp for 2 days with 2 vols NH₄ClAq (containing 13 4 g.

per litre), pure NH2HgCl was obtained André has also examined the pps obtained by adding NH₂Aq, and also NH₄ClAq, to HgCl₂Aq in presence of KOH (C R 108, 1108, 1164) The pps are compounds of NH₂HgCl, NHg₂Cl, and (NH₂ Hg₂O)Cl in varying proportions

Properties -A white solid, which volatilises completely, when strongly heated, without melt-Readily sol in HClAq, not blackened by NH3Aq, dissolved by acids, also by hot solutions

of NH, salts

Reactions -1 When heated, in an open vessel, does not melt but yields a sublimate of HgCl and a mixture of 1 vol N and 2 vols NH, $(6NH_2HgCl = 6HgCl + 4NH_3 + N_2$, Kane, A Ch [2] 72, 215)When slowly heated in a retort to o 340°, HgCl, and NH_s are given off, and a red crystalline compound, 2NHg,Cl HgCl,, re mains —2 Decomposed by water, slowly by cold, more rapidly by hot, eventually with formation of yellow mercuroxy ammonium chloride, $(NH_2 Hg_2O)Cl$, and NH_4Cl $(2NH_2HgCl + H_2O + Aq$ $= (NH_2 Hg_2 O)Cl + NH_1 ClAq) -3$ Potash or soda separates (NH₂ Hg₂O)Cl and evolves NH₃ Only half the N of the original NH2HgCl is evolved as NH, (Kane, lc), but by boiling for some days with KOHAq, renewed from time to time, all the N is removed as NH_3 , and HgO remains (Schmieder, J pr 75, 147) The fact that only half the N is readily evolved as NH₃, by the action of alkalis on NH₂HgCl, has induced Rammelsberg (J pr [2] 38,558) to regard this body as a compound of dimercuri ammonium chlor ide and NH,Cl, and to give it the formula NHg,Cl NH,Cl But it is to be remembered, as pointed out by Kane, that water readily separates NH₂HgCl into (NH₂ Hg₂O)Cl and NH₄Cl. hence the NH, obtained by the action of aqueous alkalı is probably due to the direct decomposi tion of NH Cl by the alkali—4 Boiled with very dilute sulphuric acid till dissolved, the compound HgCl 2NH Cl 2HgSO, forms on cooling (Kosman, A Ch [3] 27, 238) -5Heated in dry hydrogen chloride, HgCl, and NH,Cl are produced (Ullgren, A 26, 203)— 6 Heated with solutions of sodium chloride potassium vodide, barium sulphide, &c, NH3 14 evolved and HgCl₂, HgI₂, HgS, &c, formed, eg NH, HgCl + 2KIAq + H,O

= HgI₂ + KClAq + KOHAq + NH, (Kane, lc, Rammelsberg, P 48, 182) —7 Boiled with am monium chloride solution, mercuri diammonium chloride N.H. Hg Cl. (fusible white precipitate) is produced -8 Decomposed by heating with sulphur, with formation of a yellow sublimate of a chlorosulphide of N —9 Rubbed with soding and a little alcohol, HgI2 is formed and then an explosion occurs, probably from production and decomposition of N iodide (Rice, Ph [3] 6, 765, of Schwarzenbach, B 8, 1231, Flückiger, B 8, 619) -- 10 Bromine and chlorine cause evolution of N and formation of HgBr2 or HgCl2 (Schwarzenbach, B 8, 1231) -11 Decomposed by alcoholic iodides, e g EtI (v Sonnenschein, A 101, 20) -12 For reactin with amylic mercaptan

Wagner, J pr 53, 378

Combinations —1 Forms various compounds with NHg,Cl and (NH, Hg,O)Cl; obtained by adding NH,Aq or NH,ClAq to solutions of HgCl2Aq containing KOH (André, C R 108, 1108, 1164) -2 Combines with HgCl. to form NH, HgCl HgCl2; produced by slowly heating to

o 340° in a retort (Millon, A Ch [3] 18, 392)

Mercuri-ammonium bromide, (NH, Hg)Br
(Mercuri bromamide, or amido-mercuric bromide (Hg NH₂ Br) Dimercuri diammonium bromide (N2H4Hg2 Br2)) A yellow powder, obtained by ppg HgBr,Aq with excess of,NH,Aq (cf Mercuri ammonium chloride, supra) Insol water or alcohol, slowly changed by cold water, more quickly by hot water, to NHg2Br (Pesci, G 19, 509) E sol NH, Aq Heated gives N, NH, and HgBr, when very slowly heated to c 340° gives NH₃, HgBr₂NH₃, and NHg₂Br HgBr₂ (Mitscherlich, *J pr* 19, 455)

Series (11) pounds, NHg₂ X Dimercuri ammonium compounds, NHg₂X According to Pesci (G 19, 509) many and probably all the dimercuri ammonium salts, when digested with NH,Cl, NH,Br, or NH₄I solution, evolve NH₃ in the proportion of 4NH₃ for each NHg₂ group in the dimercuriammonium salt This reaction may be applied to estimate dimercuri ammonium salts, by conducting the digestion in a closed vessel containing a dish with a measured quantity of normal oxalic acid

Dimercuri-ammonium hydroxide, NHg OH (Mercurammonium hydroxide) Prepared by saturating yellow HgO with NH₃ under increased pressure, finely powdering, and again saturating with NH3, or by shaking HgO with alcoholic NH₃ for some hours and drying at ordinary temp in NH3 gas, the product, which is NHg₂OH H₂O, is then heated in dry NH, to 80°-85° The operation should be conducted in the dark (Weyl, P 121, 601, 131, 539) A brown powder, explodes when strongly heated, decomposed by water, with evolution of NH3, absorbs CO, from air, evolving NH3 at the same time, dissolves in warm HClAq or HNO,Aq with formation of salts of Hg and NH,

Heated to 100° in absence of air, gives dimercuri ammonium oxide (NHg)20 dark brown powder which explodes when heated, struck, or rubbed in a mortar, readily combines with water to form NHg₂OH H₂O, soluble in HClAq and HNO₃Aq, reacts with HCl gas to foim HgCl₂ and NH₄Cl. This oxide is also formed by the action of liquid NH, on HgO

hydrate of dimercuri-ammonium hydroxide NHg₂OH H₂O, 18 a yellow powder, obtained as described above appears to be isomeric with mercuroxy ammonium hydroxide (NH₂ Hg₂O)OH (p 211)

Dimercuri - ammonium chloride, NHg, Cl (Mercurammonium chloride) Obtained by treat ing the hydroxide (v supra) with alcoholic solution of HCl, also by treating the oxychloride formed by fusing together HgO and HgCl, in the ratio 3HgO HgCl₂, with liquid NH₃, and removing excess of NH₃ by warming in a stream of dry air at 150° Forms a yellow powder, de composed suddenly at 300° to HgCl, Hg, and N (Weyl, P 121, 601, 131, 529). Not acted on by boiling water, decomposed by hot KOHAq with production of NH, and HgO; slowly dissolved by cold HClAq

Forms a double compound with mer-curic chloride 2NHg. Cl. HgCl. (dimercurs-ammonium-mercurs chloride). A red crystalline solid, resembling HgO, produced by very slowly Vol. III

heating mercuri ammonium chloride, NH, Hg Cl, in a retort until HgCl begins to sublime compound reacts with hot HClAq to form NH,Cl and HgCl₂, it is said to be unchanged by conc HNO,Aq, dilute H₂SO,Aq, H₂O, or boiling alkali solutions (Mitscherlich, *J pr* 19, 453) Heated to 360° it separates into N, HgCl, and Hg

Dimercuri - ammonium bromide, NHg.Br (Mercurammonium bromide) Obtained by ppg HgBr,Aq by excess of NH, Aq and digesting the pp (NH,HgBr) with water, better, by adding excess of NH, carbonate to HgBr,Aq, washing the pp of 4NHg2Br 5NH4Br with NH4 carbonate, warming with KOHAq, and washing with cold water (Pesci, G 19, 509) Also obtained, according to Pesci, by the action of dilute HBrAq on Millon's base (NH₂Hg₂O)OH A yellow powder, insol water, sol HClAq, insol HNO,Aq, decomposed by heat, without melting, yielding NH3 and a sublimate which contains Hg (Pesci, Digested for a short time with boiling NH, BrAq, and filtered, small crystals of NHg, Br 3NH, Br are obtained This compound seems similar to fusible white precipitate, it is described on p 210 as mercuri diam monium bromide. The double compound 4NHg, Br 5NH, Br is obtained, in clear microscopic needles, by adding excess of NH, car bonate to HgBr₂Aq (Pesci, lc)

Dimercuri ammonium iodide, NHg2I, is ob tained by the action of liquid NH, on the oxy iodide formed by fusing together HgO and HgI_2 in the ratio $3HgO HgI_2$ (Weyl, P 121,601, 131, 539)

Dimercuri ammonium selenate,

(NHg₂)₂SeO₄ 2H₂O A white pp which darkens in light and is decomposed by heat; obtained by dissolving the basic selenate HgSeO, 2HgO in cone NH, Aq, and ppg by much water (Cameron a Davy, C N 44, 63)

Series (111)
pounds, N.H. HgX. Mercuri diammonium com

Mercuri-diammonium chloride, N2H6Hg Cl2 (Mercurammonium chloride Fusible white Ammonio mercuric chloride. precipitate $HgCl_2 2NH_1$) Rammelsberg (J pr [2] 38, 558) regards this salt as a double compound of di chloride-NHg2Cl-and mercuri ammonium chloride—NHg₂Cl—and NH₄Cl He formulates it as NHg₄Cl 3NH₄Cl (v infra)

When an alkalı carbonate is added to HgCl₂Aq containing NH₄Cl, a white pp is ob tained, this pp was called in pharmacy mercurius precipitatus albus, and for long was supposed to be the same as that formed by adding NH,Aq to HgCl2Aq Wöhler (P 26, 203) found that the pp formed by alkalı carbonate, in presence of sal ammoniac, melted when heated, before volatilising, but that the pp formed by ammonia volatilised without melting former pp was then called fusible white precipitate, to distinguish it from the latter to which the name infusible white precipitate was given

The researches of Krug (Ar Ph 42, 1) have shown that pure mercuri diammonium chloride cannot be obtained by addition of alkali car bonate to HgCl_Aq containing NH_Cl at the ordinary temperature, the pp consists of a mix-ture of mercuri ammonium chloride (infusible white precipitate, NH.Hg Cl) and mercuri-diammonium chloride (fusible white precipitate, N2H2H2 Cl2), the longer the pp remains in contact with the supernatant liquor, and the higher the temperature, the greater is the amount of fusible white precipitate formed Krug found that almost pure NH, HgCl (infusible white precipitate) was obtained by adding Na₂CO₃Aq to HgCl₂Aq mixed with NH₂Cl at 0°, and filtering at once (about 4Na₂CO₃HgCl₂9NH₂Cl) The first pp formed by the alkalı carbonate therefore probably always consists mostly of mercuri ammonium chloride, NH2Hg Cl, but this is acted on by the NH₄Cl present, and thus more or less N₂H₆Hg Cl₂ is produced, CO₂ is also given off from the alkali carbonate used, and this CO₂, according to Krug's experiments, seems to change some of the NH2HgCl to HgCl, xHgO (with simultaneous formation of NH₄Cl and NH₄HCO₂), which oxychloride then probably reacts with

NH₄Cl to produce N₂H₆Hg Cl₂
Preparation —HgCl₂Aq is dropped into boiling NH ClAq containing NH3, as long as the pp which forms is redissolved, and the liquid is allowed to cool The compound crystallises out ın garnet red dodecahedra Melts at c 300°

with decomposition

Properties and Reactions - Small red dodecahedra, also formed by ppn with Na₂CO, as a white powder Gently heated, gives off half its NH_s , leaving $HgCl_1NH_s$ (v infra), melts at c 300°, evolving N and NH_s and yielding a sublimate which reacts with water to form NH₄Cl, HgCl₂, and HgCl Boilingreacts to form mercuroxy ammonium chloride, (NH₂ Hg₄O)Cl, and NH₄Cl Alkalis evolve NH₃ According to Rammelsberg (J pr [2] 38, 558) three fourths of the N of mercuri diammonium chloride is evolved by the action of hot alkali solution, hence R assigns to this compound the formula NHg,Cl 3NH,Cl, but as the action of boiling water on N2H6Hg Cl2 is to produce (NH₂Hg₂O)Cl and NH₄Cl in the (NH, Hg,O)Cl 3NH,Cl, it is easy to account for the action of boiling alkali without suppos ing fusible white precipitate to be a double compound of NHg₂Cl with NH₄Cl Iodine reacts energetically, according to Fluckiger (B 8, 1619) the reaction is expressed thus $6(N_2H_6Hg Cl_2) + 2I_2$ $= N_2 + 6NH_4Cl + 4NH_3 + 2HgCl_2 + 2HgI_2 + 2HgCl$ Liquid ammonia dissolves N2H2HgCl2, after prolonged action, and evaporation of the excess of NH2, a white crystalline mass remains which has the same composition as the original, ac-

cording to Weyl (P 1, 547)

Combination — The compound HgCl₂ NH₂

may be regarded as a compound of N,H₄Hg Cl₂ with HgCl₂ [N₂H₆Hg Cl₂ HgCl₂ = 2(HgCl₂ NH₃)] This compound is formed by heating HgCl, in dry NH, or by distilling HgO with NH,Cl, it melts when heated and distils without much change, it is decomposed by water, forming NH, Hg Cl and HgCl, NH, Cl (Kane, A Ch [2]

72, 215)

Mercuri-diammonium bromide, N2H4Hg Br2 Small microscopic, rhombohedral, transparent crystals, obtained by adding excess of NH, carbonate to HgBr,Aq, boiling the 4NHg2Br 5NH4Br for a short time with NH4BrAq, filtering, and allowing to cool (Pesci, G 19, 509) Also formed by treating dimercuri ammonium bromide (NHg.Br) with boiling NH.BrAq, by

the action of NH, Aq on solution HgBr, NH, Br; also by adding alcoholic NH, to HgBr, dissolved in alcohol (P, lc) Melts at c 180° with evolution of NH, more strongly heated, yields two distinct sublimates Easily sol HClAq, H_SO,Aq forms HgBr2, alkalıs produce NHg,Br (P, lc) Forms a compound with HgBr. N₂H₈Hg Br₂ HgBr₂(=HgBr₂ NH₃) similar V1Z to the chloro compound already described (H Rose, P 20, 160)

Mercuri-diammonium sulphate,

N₂H₆H_g SO₄ H₂O Lustrous, orthorhombic, crystals Obtained by adding, little by little, yellow HgO to pure, saturated, cold (NH₄), SO₄Aq, each portion of HgO being allowed to dissolve before another portion is added, the liquid being kept cold, addition of HgO is continued till the liquid begins to grow turbid, the clear liquid is decanted and allowed to evaporate in the air or in vacuo This compound is decomposed by the smallest quantity of water with production of a compound of mercuroxy ammonium sulphate and mercuri ammonium sulphate,

$3(NH_2Hg_2O)_2SO_4(NH_2Hg)_2SO_4$

boiling water removes more H2SO4, finally form ing (NH, Hg,0),SO₄ (v Mercuroxy ammonum sulphate, p 211, cf Millon, A Ch [3] 18, 410, Schmieder, J pr 75, 147) It is e sol in (NH4)2SO4Aq, NH4ClAq, HClAq, dilute H2SO4Aq, and HNO, Aq, insol conc HNO, Aq with cone H2SO4 it gives (NH4)2SO4 and HgSO4, decomposed by KOHAq, forming a basic compound, with boiling cone KOHAq, NH, is evolved and HgO formed Heated to 115° water is evolved, and at a higher temperature complete decomposition results

Mercuri-diammonium iodide N₂H₆Hg I₂, Mercuri diammonium fluor ide N₂H₆Hg F₂, and the double compound N₂H₆Hg I₂ HgI₂, have been described (v. H. Rose, P 20, 160, Nessler, C C 1856 530, Finkener, P 110, 147, Rammelsberg, P 48, 170, Caillot a Carriol, J. Ph 9, 381)

Series (1V) Dimercuri diammonium compounds , $N_2H_4Hg_2X_2$

Dimercuri-diammonium sulphate, $N_2H_4Hg_2SO_4H_2O$ (= $SO_22HgO2NH_2$) Obtained, according to Millon (A Ch [3] 18, 410), by saturating 70 c c cold cone NH_2Aq with $HgSO_4$. allowing to stand in an atmosphere of NH₃ over CaO for some months, powdering the crystals which separate, and drying over CaO

Series (v) Trimercuri diammonium com pounds, $N_2H_2Hg_3X_2$

Trimercuri diammonium sulphate $N_2H_2Hg_3SO_42H_2O$ (= $SO_38HgO2NH_2$) pared similarly to preceding salt, but using 90 c o NH, Aq (Millon, lc)

Class III MERCUROXY AMMONIUM COMPOUNDS

(NH₂ Hg₂O)X.

The name mercuroxy- is here given to the group Hg₂O, which s supposed to act as a dyad The salts of this radicle in these compounds series may be regarded as hydrated tetramercuridiammonium compounds, thus the carbonate (NH₂·Hg₂O)₂CO₂ may be written N₂Hg₄ CO₂ 2H₂O, and the chloride (NH₂ Hg₂O)Cl may be written N.Hg, Cl, 2H,O Some of the salts of this series may also be regarded as hydrated dimerouriammonium compounds, thus the chloride (NH₂ Hg₂O)Cl loses water at 200°, and is there fore regarded by Rammelsberg as NHg₂Cl H₂O

Mercuroxy-ammonium hydroxide,

(NH₂ Hg₂O)OH (Millon's base) This is the final product of the reaction of NH, Aq on HgO, the hydroxide contains H₂O Millon gave the formula NH₂ Hg₂O OH H₂O, Gerresheim, the formula 2(NH₂ Hg₂O OH) H₂O (A 195, 373), and Rammelsberg, more recently (J pr [2] 38, 558), assigns the composition 3(NH₂ Hg₂O OH) 2H₂O The empirical formula for the base is 2HgO NH₂xH₂O

Preparation —Yellow HgO is agitated with NH₃Aq, quite free from carbonate, so long as any change occurs, if red HgO is used the change is not completed for some days. The yellow brown product is washed with cold water, crystallised from hot water, and dried (Millon,

A Ch [3] 18, 392)

Properties — Yellow, microscopic crystals, probably rhombic Appears to be isomeric with hydrated dimercuri ammonium hydroxide NHg,0H H,O (p. 209) Insol alcohol or ether, somewhat sol water S 007 at 17°, 06 at 80° Acts as a very strong base, decomposes NH, salts energetically with evolution of NH,, and rapidly combines with CO₂ when exposed to air Several salts may be obtained by dissolving the base in excess of acetic acid, and ppg by alkali permanganate, chromate, &c Over H,SO₄ loses H₂O and becomes brown, heated to 130° further loses ½H₂O, leaving mercuroxy ammonium oxide (NH, H₂O).0

oxide (NH₂ Hg₂O),O

Reactions—1 The hydrated base is very slowly decomposed by boiling alkali solution, the dehydrated base is only decomposed by molten alkali—2 Decomposes ammonium salts rapidly, with evolution of NH₃—3 Combines so rapidly with carbon dioxide that it is almost impossible to obtain the base quite free from carbonate—4 With acids forms salts (NH₂ Hg₂O)X (X = NO₃, ¹SO₃, &o) (v Rammels berg, J pr [2] 38, 558)—5 Decomposed by heat with more or less explosion (Millon, lc, c, fHirzel, J 1852 419, 1853 381)—6 Many salts, e g sulphates and chlorides, are decomposed by shaking with Millon's base, with complete re moval of the acid of the salt used (v Gerres heim, A 195, 373)—7 Heated with ethylic iodide to 100° yields crystals of 2NEt,I 3HgL, ethylic bromide reacts similarly—8 A thic carbonate of the base is obtained by heating with carbon dissulphide (Gerresheim, Ic)

Mercuroxy ammonium chloride,

mercurvy ammonium chloride, (NH₂ Hg₂O)Cl (Hydrated tetramercurammonium chloride N₂Hg₂Cl₂ 2H₂O Hydrated dimercuri ammonium chloride NHg₂Cl H₂O) This compound is formed by the reaction of boiling water with either fusible white pp N₂H₆Hg Cl₂ or infusible white pp NH₂Hg Cl It is also produced by passing dry NH₂ over the oxychloride SHgO HgCl₂ at 150° (Uligren, P 42, 395) A heavy, yellow powder, v s' sol water, e sol HClAq and HNO₂Aq (Kane, P 42, 367) Decomposed by heat, giving NH₃, N, H₂O, HgCl, and Hg Decomposed by excess of solutions of KCl, NaCl, and KI, with evolution of NH₃ Loses water at 200°, and is therefore regarded by Rammelsberg as NHg₂Cl.H₂O (J. pr. [2] 88, 559).

Mercuroxy-ammonium chloride combines with NH₂HgCl and NH₂Cl to form various double compounds, eg $3(NH_2Hg_2O)Cl NH_2HgCl$

3(NH, Hg,O)Cl NH,HgCl and (NH Hg,O)Cl NHg Cl,

these compounds were obtained by André by ppg HgCl₂Aq with NH₃Aq, some of them requiring the presence of KOH for their production (O R 108, 233, 290, 1108, 1164)

Mercuroxy ammonium iodide, (NH, Hg,O)I. (Hydrated tetramercurammonium iodide N,2Hg, I, 2H,O Hydrated dimercura ammonium iodide NHg,I L, 2H,O Hydrated dimercura ammonium iodide NHg,I H,O) This compound is formed by adding NH,3Aq to Nessler's reagent (alkaline solution of HgI, in KIAq), the composition of the pp thus produced is often represented as Hg NH, I+HgO, or as Hg NHg I+HO The compound is best prepared by dissolving HgI, 2KI in KOHAq, adding NH,Aq, washing thoroughly with cold water, and drying at 100°

 $\begin{array}{c} (2K,HgI_4Aq+3KOHAq+NH,Aq\\ = (NH_2Hg_0)I+7kIAq+2HO,\\ v \ \ Rammelsberg,\ P\ 48,\ 170) \ \ (NH\ Hg_2O)I\ is\\ also formed by heating 3HgO\ HgI_1\ to\ 180^\circ\ in\\ NH_1\ (Rammelsberg),\ and\ by\ boiling\ HgI_2\ with\\ excess of cono\ NH_3Aq \end{array}$

Mercuroxy ammonium iodide is a brown powder with a puiple red tint. Begins to give off water at 128°, heated more highly, out of contact with air, it melts to a dark brown liquid, and then decomposes violently, giving HO, Hg, HgI., NH, and N Sol warm KIAq, with formation of K HgI. and KOH and evolution of NH, Sol warm HClAq, HgI. and HgICl are deposited on cooling (R immelsbeig). Decomposed by hot BaSAq, with evolution of all N as NH, Heated in HCl gas, gives a sublimate of HgCl., NH,Cl, NH,I, and (NH,) HgI.

Mercuroxy ammonium nitrates Several nitrates, and some double nitrates, of the mer curoxy ammonium compounds seem to exist

The salt often called Souberran's ammo natcal salt is probably the normal nitrate (NH, Hg O)NO, (Souberran, J Ph 12, 465) This compound is obtained by ppg dilute Hg(NO₄), Aq, containing only a little free acid, with very dilute NH, Aq, boiling with water till the pp becomes compact and curdy, washing, and drying

The loose flocculent pp produced by adding very dilute NH,Aq to dilute Hg(NO₃).Aq, sometimes known as Mischerlich's ammoniacal salt, is probably a double compound of mercuroxy ammonium nitrate and mercuri ammonium nitrate.

and mercuri ammonium ni (NH₂ Hg₂O)NO₃ (NH Hg)NO₄ H₂O

Other compounds are obtained by boiling Mitscherhich's salt with excess of NH₂Aq with addition of NH₂NO₂Aq, and by dissolving Souberran's salt in hot cone NH₂NO₂Aq, the salts thus formed are probably double compounds of mercuroxy ammonium nitrate and ammonium nitrate, but their exact composition and constitution are not yet decided (v Mitscherhich, P 9, 387, 16, 41, Millon, A Ch. [3] 18, 392, Kane, A Ch [2] 72, 215, Nessler, J 1856 409)

Merouroxy-ammonium sulphate, (NH₂ Hg₂O)₃SO₄ (Hydrated tetramercuram-monum sulphate, N₂Hg₄SO₄ 2H₂O₅ Hydrated domercuri-ammonium sulphate,

(NHg.)₈SO₄ 2H₂O Ammoniacal turpethum) Obtained by saturating cone NH₂Aq with HgSO₄, also by digesting the basic sulphate HgSO₄. HgO (mineral turpethum) with NH₂Aq, also by digesting HgO with hot (NH₂)₂SO₄Aq (Millon, A Ch [3] 18, 392, Ullgren, P 42, 395, Hirzel, J 1852 419, 1853 381) Schmieder (J pr 75, 147) obtained the salt by repeatedly treating mercuri-diammonium sulphate, N₂H₂HgSO₃ HO (v p 210), with boiling water, till the filtrate was free from sulphates Forms a heavy yellow white powder, sl sol water, easily sol HClAq or HNO₂Aq Decomposed by heat to H₂O, N, NH₃, and Hg₃SO₄ Treated with KOHAq, gives NH₂ and a basic salt (NH₂Hg₂O)₂SO₄HgO (perhaps NH₂Hg₂O NH₂Hg₃O SO₄), and on further treatment with KOHAq yields NH₃, HgO, and K₂SO₄

Besides the mercuroxy ammonium salts de scribed above, the following have been pre

Mercuroxy ammonium bromate (NH₂Hg₂O)BrO₂ (Rammelsberg, P 55, 82)

Mercuroxy ammonium carbonate (NH₂ Hg₂0),CO₃ (Millon, A Ch [3] 18, 392, Hirzel, J 1852 419, 1853 381)

Mercuroxy ammonium chromate (NH₂ Hg₂O)₂CrO₄, and a double basic salt (NH₂ Hg₂O)₂CrO₄ 3HgCrO₄ HgO (Hirzel, lc)

Acid mercuroxy ammonium fluoride (NH₂ Hg₂O)F HF (Finkener, P 110, 632)

Mercuroxy ammonium - ammonium sodate (NH₂Hg₂O)IO₃ 2NH₄IO₃ (Millon, A Ch [3] 18, 410)

Mercuroxy ammonium - mercuric phosphate (NH₂ Hg₂O) Hg PO₄ (Hirzel, J 1852 419, 1853 381)

Mercuroxy - ammonium - mercuric sulphite (NH₂ Hg₂O)₂SO₃ HgSO₃ (Hirzel, lc) M M P M

MERCURIALINE The volatile base ob tained by distilling the seeds of Mercurialiss annua or M perennis with lime and water, and formerly called 'mercurialine,' is identical with methylamine (E Schmidt, B 10, 2226, A 193, 73. cf Reichardt, J. rr. 104, 301)

73. cf Reichardt, J pr 104, 301

MERCURY (Quicksilver**) Hg At w
199 8 Mol w 199 8 [- 38 5°] (Regnault, Acad 26, 525) [- 38 85°] (Mallet, P M [5]
4, 145) (357 25° at 760 mm) (Regnault, I c , for table of B P of Hg at pressures from 123 to 798 mm v Ramsay a Young, C J 47, 656)

**S G \(^{\text{op}}_{\overline{D}}\) 13 546

**Volkmann, W 13, 209 , a very full table of S G and volume of Hg from 0° to 360° is given)

**S G solid Hg, \(^{\text{sol}}\) 20 3 at 440° to 1565° (V Meyer, B 12, 1426) S H 03312 from 20° to 50°, 03278 from 25° to 142° (Winkelmann, P 159, 152, v also Pettersson, B 12, 1718)

**S H p \(^{\text{S}}\) 75° to 356° = 1 666 (Kundt a Warburg, P 157, 353, experimentally determined) C E 00018153 from 0° to 100° (Regnault, Acad 21, 271, v also Wällner, P 153, 440) T O (Ag = 100) 5 3 (Calvert a Johnson, P M [4] 16, 881, cf Weber, W 10, 490) E C c 196 (Ou = 100) For electrical resistance of Hg v

Kohlrausch, W 35, 700, (cf Giunmach, W 37, 508) For table of vapour pressures of Hg from 1.35° to 520° v Ramsay a Young, C J 49, 37 Heat required to change 200 grm Hg at 358° to gas = 12,400 gram calories, heat required to melt 200 grm solid Hg = 564 (Person, A Ch [3] 24, 257, 4bul 21, 295) Chief lines in emission spectrum 6151, 5460 5, 4358 (Thalón, 1868, for table of lines of ligh refrangibility v Hartley a Adeney, T 1884 \$136) S V S c 14 Crystal lises in regular octahedra

Occurrence—Small quantities of Hg are found as globules disseminated through ores of Hg, or in the rocks in which these ores occur. The chief ore of Hg is cinnabar, HgS, found in limited quantities in Illyria, Spain, Bohemia, Peru, China, California, the Ural, and one or two other localities. An amelgam of Hg and Ag is sometimes found native, iodide, chloride, and minute quantities of selenide, of Hg are also known to occur.

Preparation—1 By distilling cinnabar in a regulated supply of air, condensing the Hg in a suitable apparatus, and allowing the SO₂ to escape—2 By heating cinnabar with lime, CaS and CaSO₄ are formed, and the Hg distils and is condensed—8 By heating cinnabar with iron (smithy scales), Hg, FeS, and SO₂ are produced, the Hg is condensed in long chambers, or by downward distillation in a trough filled with

water To purify Hg from dust, &c, it may be filtered through a paper cone having a minute hole at the apex, or pressed through leather Traces of metals in solution may be removed by leaving the Hg in contact with cold conc H.SO for some weeks, with frequent agitation, and then digesting with very dilute HNO,Aq, or with HgNO₃Aq (Branchi, R P 6, 77, Wittstein, R P 65, 362) Karsten and Ulex (A 60, 210) re commend to rub the Hg in a basin for ten minutes, with 1 60th of its weight of FeCl, Aq, S G 148 diluted with an equal weight of water. to pour off the liquid, which contains the foreign metals and some HgCl₂, to wash with water, and then to dry the Hg by heating it L Meyer (B 12, 437) has described a convenient apparatus for purifying Hg by bringing a fine stream of it into contact with FeCl, Aq Bruhl (B 12, 204) shakes Hg with an equal volume of chromate solution, made by dissolving 5 grams K,Cr,O, in 1 litre water, and adding a few c c of H,SO, the shaking is continued until the red HgCrO at first produced has disappeared, and the liquid is coloured green by $\operatorname{Cr}_2(\operatorname{SO}_4)_2$, the fine greyish powder which is formed, and which consists of oxides of foreign metals, is washed away by a rapid stream of water The process is repeated. and the Hg is then shaken with pure water until no more greyish powder is formed About half pe of Hg is lost Crafts (Bl [2] 49, 856) removes Pb, Zn, Sn, and most other metallic impurities from Hg by placing the Hg in a slightly inclined glass tube, and aspirating a gentle current of air through the apparatus for about forty eight hours. The oxides of the foreign metals collect at the top Ag cannot be be removed by this method

Pure Hg may be obtained by distilling equal parts of cinnabar and burnt lime or Fe filings. Also by boiling pure HgCl.Aq with pure Fe.

Also by heating HgO in a retort, and digesting the residual Hg, which contains a little HgO, with dilute HNO₂Aq or H₂SO₄ Millon (B J 27, 110) prepares HgO (from which to make Hg) by shaking Hg for some time with dilute HNO, Aq to remove foreign metals, washing, dissolving in such a quantity of HNO, Aq that 1 10th of the Hg remains undissolved, evaporating to dryness, and heating

After purifying Hg by one of the foregoing methods it is advisable to distil it A very con venient apparatus for distilling Hg under reduced pressure is described by Wright (Am S [3] 22, 479, v also Weber, Carl Rep 15, 52, Weinhold, Carl Rep 15, 1)

Properties -A very lustrous metal, white, with the slightest tinge of blue Exists as a very mobile liquid at ordinary temperatures, and does not solidify above - 38 5° Hg boils at c 360°, but it is very easy volatilised, even at -13° sufficient Hg is vaporised to produce a daguerrectype by twenty four hours' exposure (Regnault, \hat{C} R 73, 1462) According to Merget (C R 73, 1386) solid Hg at -44° is very slowly Solid Hg is a tin-white, ductile mass of octahedral and needle shaped crystals It may be cut with a knife Hg is a very coherent liquid By trituration with sugar, grease, sulphur, chalk, &c, or by agitation with ether, turpentine, and some other liquids, Hg ap pears as a grey powder, which consists of minute globules of Hg separated by the foreign matter present (extinction or deadening of mer Finely divided Hg is also obtained by mixing about equal parts of SnCl2, dissolved in HClAq, and HgCl2 dissolved in hot water $(\operatorname{SnCl}_2\operatorname{Aq} + \operatorname{HgCl}_2\operatorname{Aq} = \operatorname{SnCl}_4\operatorname{Aq} + \operatorname{Hg})$ In this state of fine division, Hg is slowly oxidised by contact with air Pure Hg adheres very slightly to glass When foreign metals are present the Hg leaves a blackish film on glass A globule of pure Hg should roll down a slightly inclined surface without losing its round form, and with out leaving any streak behind it When shaken in a bottle with dry air it should not form any black powder

Pure Hg is not oxidised by exposure to air at ordinary temperatures, when heated to near its BP, HgO is slowly formed [Berthelot (C R 91, 871) asserts that pure Hg is very slightly Hg obtained in a state of fine oxidised in air] division by trituration, eg with chalk, is slowly oxidised at the ordinary temperature. Ozone oxidises Hg at ordinary temperatures (Volta, G 9, 521, cf Reactions, No 2) Hg combines directly with O, S, and the halogens, it alloys with most of the metals, in some cases forming definite compounds (v Mercury, amalgams of) Hg reacts with hot cone H.SO, to produce HgSO, and SO₂, with HNO, Aq it produces HgNO, Hg(NO₃)₂, or a basic nitrate, according to the temperature and the quantity of acid does not react with Hg

The atomic weight of Hg has been determined (1) by analysing HgO (Sefström, S 22, 328, Turner, A 13, 18, Erdmann a Marchand, J pr 31, 895), (2) by determining Cl in HgCl and HgCl₂ (Turner, Ic, Svanberg, J pr 45, 468, Millon, A Ch [3] 18, 345), (3) by estimating Hg in HgS (Erdmann a Marchand, J. pr 81, 400), (4) by determining S H of Hg.

Hg is distinctly a metallic element. It forms salts by replacing the H of most acids These salts belong to two series, HgX and HgX_2 , where $X = NO_2$, ClO_2 , $\frac{1}{2}SO_4$, $\frac{1}{2}PO_4$, &c Both series are well represented by definite and stable salts HgO dissolves in molten KOH, and crystals of K₂O HgO are obtained on cooling pound Na₂O HgO is said also to exist HgS dissolves in NaHSAq and cone KHSAq The com pound K2S HgS 5H2O has been isolated The existence of these compounds shows that HgO and HgS are slightly acidic towards K.O and KHS

The molecular weight of Hg has been directly determined, the molecule is monatomic atom of Hg is divalent in the gaseous molecules HgCl₂, HgBr₂, and HgI₂ The molecular formula of calomel 1s probably HgCl, if this 1s so, the atom of Hg is monovalent in this molecule

Hg is related to Mg and Zn, and more dis tantly to Be, Ca, Sr, and Ba (v MAGNESIUM GROUP OF ELEMENTS, p 165, and of CLASSIFICA-TION, vol 11 pp 204, 207)

Reactions—1 Heated in air or oxygen, to

near its BP, Hg slowly forms HgO -2 Ozone produces some Hg₂O at ordinary temperatures, perfectly dry ozone does not react with dry Hg (Shenstone a Cundall, C J 51, 619) —3 Hg is oxidised by agitation with solution of potassium permanganate, Hg2O is formed if the solution is cold, and HgO if hot (Kirchmann, Ar Ph [2] 150, 203) -4 Hg does not react with hydro chloric acid -5 Sulphuric acid, when hot and cone, forms HgSO4, or Hg2SO4 if there be an excess of Hg and the acid is not very hot, and SO₂, dilute H₂SO₄Aq scarcely acts on Hg -6 Nitric acid, cold and dilute, forms HgNO, , with hot HNO, Aq and excess of Hg, basic mercurous nitrates, $x Hg_2 O y N_2 O_5$, are formed, excess of hot HNO_3Aq produces $Hg(NO_3)_2$ —7 Warm cone hydrobromic and hydriodic acids produce HgBr. and HgI2, respectively (cf Berthelot, A Ch [5] 16, 433) —8 Hydrogen sulphide, or alkaline polysulphides, produce HgS —9 With nitrogen tetroxide, forms HgNO, and NO (Ramsay, B 18,

Combinations — 1 Hg combines with the halogens, forming Hg X or HgX₂ according to the relative quantities of the reacting bodies -- 2 With oxygen, Hg forms Hg₂O and HgO -3 With sulphur and selenton, HgS and HgSe are produced -4 Hg probably combines with phos-phorus, but no definite compound has been iso

lated with certainty

Detection and Estimation - Solid Hg com pounds are decomposed by drying, mixing well with dry Na, CO,, and heating strongly in a small tube closed at one end, Hg is volatilised, and condenses on the cold part of the tube in minute globules Mercurous salts in solution give a white pp (HgCl) with HClAq, or a soluble chloride, this pp is blackened by NH₄Aq with formation of NH₂Hg₂Cl Mercurous salts are oxidised to mercuric salts by boiling with HNO, Aq. Mercuric salts are not ppd by HClAq H.SAq, or a soluble sulphide, ppts black HgS, addition of a small quantity of the reagent causes the formation of a compound of HgS with the original salt present, this pp is white, yellow, or brown, according to the quantity of reagent

Hg is sometimes estimated by heating its dry compounds with powdered CaO, condensing the Hg under water, transferring to a weighed crucible, drying by blotting paper and then over H₂SO₄, the metal is sometimes ppd by SnCl₂ or H.PO.Aq at c 60°, dried, and weighed is also estimated as HgCl, by adding HClAq, then nearly neutralising with KOHAq, adding K or Na formate, digesting for some days at 60°-70° (Hg is ppd at boiling temperature), collecting the HgCl on a weighed filter, washing, drying at a low temperature and weighing 18 also determined as HgS, by ppn from HgCl₂Aq by H,S, and collection on a weighed filter the pp is formed from solutions containing HNO, Aq or FeCl, Aq &c, free S is ppd with the HgS, the pp may then be heated with CaO and the Hg collected, or heated in Cl, the HgCl2 passed into water, and Hg ppd by SnCl₂ Hg may also be determined by depositing it by electrolysis on a weighed Pt dish A mercurous salt, in presence of mercuric, may be estimated by ppg by HClAq, from a cold very dilute solution, not more than a very small quantity of HNO, being present

There are several methods for the volumetric determination of Hg, that described by Hannay, which is based on the fact that the turbidity produced in mercuric salt solutions by a few drops of NH, Aq is removed by a definite quantity of KCNAq, is said to give satisfactory results (For details of the methods v Manuals of

Analysis)

Mercury, alloys of, v next line Mercury, amalgams of The alloys of Hg are usually called amalgams, the word is supposed to be an alchemist's anagram of μάλαγμα = a soft mass Amalgams are known of most of those metals which have been fairly well studied Amalgams are formed by mixing the other metal with Hg, by ppg the other metal on Hg (or Hg on the other metal), and by placing the other metal in contact with Hg and a dilute acid Many amalgams are definite compounds, others seem to be merely solutions of metals in Hg, and others are probably solutions of definite com pounds in excess of Hg Amalgams of Bi, Pb, Sn, and Zn, for instance, retain Hg at 360° (B P of Hg), but not at 410° Crystalline amalgams of K and Na, K,Hg and Na,Hg, are obtained by heating solutions of K and Na in Hg to 440°

The best known amalgams are those of Al, Ba, Bı, Cd, Cs, Ca, Cr, Co, Cu, Au, Fe, Pb, Mg, Mn, Nı, Os, Pd, Pt, K, Ag, Na, Sr, Tl, Sn, and For brief accounts of these amalgams, with the exception of those of Cu which are described below, v the various metals, Aluminium, BARIUM, &c, the articles, Amalgams, vol 1 p 149, and Alloys, vol 1 p 132, should be consulted An interesting paper on Amalgams, by Dudley, will be found in Proc Amer Ass for Advancement of Science, 1890 145

COPPER AMALGAMS (should have been described under COPPER, ALLOYS OF, vol 11 p 254) Amal gams of Ou are formed by placing Cu foil in HgNO₃Aq, by triturating 3 parts Hg with a mixture of 1 part very finely divided Cu and a few drops of HgNO, Aq, by triturating Hg with NaCl and verdigris, by making Hg the negative elec trode during electrolysis of CuSO₄Aq, by immersing Na-amalgam, or Zn amalgam, in

CuSO, Aq, and in some other ways By dissolving Cu in Hg, and removing excess of Hg by pressure, Joule obtained an amalgam having the composition CuHg (Chem Gazette, 1850 339) By heating amalgams rich in Hg, De Souza obtained Cu₁₆Hg at c 410°, and Cu, Hg at c 360° (B 9, 1050) By ppg Cu from CuSO Aq Ly Fe, washing well, moistening with HgNOsAq, and rubbing with Hg, amalgams are obtained which harden after a time The amalgam with from 25 to 83 pc Cu, may be obtained soft and plastic by heating nearly to 360°, and kneading for some time in a warm mortir, this amalgam slowly hardens without either contracting or expanding, it is used for stopping teeth (v Von Gersheim, A 70, 344)

Mercury, ammonio compounds of; v Mer

CURAMMONIUM COMPOUNDS, p 206

Mercury, antimonates of, v vol 1 pp 285-6

Mercury, antimonide of A substance of the nature of an amalgam is formed by triturating together Sb and Hg, little is known of its composition and properties, it is very easily decom-

Mercury, arsenates of, v vol 1 p 309

Mercury, arsenide of Bergmann obtained what he thought was a compound of 1 pt As with 5 pts Hg by heating Hg and As together

Mercury, arsenites of, v vol 1 p 306 Mercury, bromides of Two bromides of Hg are known, HgBr and HgBr, Mcrcuric bromide has been vaporised, its mol w is 359 3 = HgBr, Mercurous bromide has also been vaporised, the results indicate the mol w 279 55 = HgBr, but it is not certain whether partial dissociation into HgBr, and Hg occurred during vaporisation (v infra, also Mercurous chloride, p 215) Both HgBr and HgBr, form double compounds with the bromides of metals more positive than Hg

MERCUROUS BROMIDE HgBr (Mercury proto or mono bromide) Mol w 279 55 (?) H F [Hg,Br] = 25,475 (Thomsen, Z P C 2,21)

Preparation -1 By subliming an intimate mixture of 80 pts Br and 200 pts Hg -2 By adding KBrAq to HgNO₃Aq -3 By heating saturated HgNO,Aq, as free as possible from HgO and slightly acidified with HNO, Aq, with Br, decanting, and allowing to cool in the dark (Stroman, B 20, 2818) -4 By adding alcoholic solution of Br to cold cone HgNO, Aq (Stroman,

Properties and Reactions - As prepared by method 3 (supra), forms small, white, nacreous, tetragonal, scales, prepared by method 2, appears as yellow, crystalline, spangles (Stroman, lc) SG 7307 (Karsten, S 65, 394) Sublimes at 340°-550° Melts c 405°(?) (Car Sublimes at 340 -500 Method 227 (1) method 227 (2) solves HgBr with evolution of SO₂, dissolves slowly in hot HNO₂Aq S G 142, decomposed by hot HClAq dil or conc, decomposed by NH,Aq or KOHAq, forming NH,Br or KBr, and leaving a black r sidue which contains Hg (Stroman, lc) Slowly decomposed by boiling KBrAq, giving HgBr, and Hg Soluble in some NH, salt solutions

Combinations -Two compounds with strontrum chloride are described by Löwig (P 14, 485) By dissolving HgBr in boiling SrBr.Aq. allowing

to cool, pouring off from separated HgBr, and evaporating, crystals of 6HgBr SrBr2 separate, by dissolving these crystals in water, filtering from HgBr which separates, and evaporating, a very soluble crystalline compound 2HgBr SrBr, 18 obtained

MERCURIO BROMIDE HgBr₂ (Dibromide of 859 3 H F [Hg,Br²] W Mercury) 859 3 Mol

= 41,880 (Thomsen, Z P C 2, 21)

Preparation — 1 By dissolving HgO in HBrAq, and crystallising -2 By bringing Hg into slight excess of Br, warming to remove un-combined Br, and subliming -3 By heating an intimate mixture of HgSO, with rather more than its own weight of KBr, the HgBr, which sublimes is said to contain HgBr -4 By adding KBrAq to Hg(NO₃)₂Aq, evaporat ng as long as HgBr₂ crystallises out, and crystallising from alcohol -5 By agitating Hg with water, adding Br as long as its colour is removed, boiling, filtering, allowing to crystallise, and drying at c 150° -6 By adding excess of Br to a slightly acid solution (S G 1 197) of Hg(NO₄)₂, HBrOAq is formed in the reaction (Sievers, B 21, 647)

Properties — White rhombic prisms, isomorphous with HgCl_2 , $a\ b\ c=6817\ 1\ 9975$ (Hjord thal, $Z\ K=3$, 362) SG 5 9202 (Karsten, S 55, 304), 5 7298 at 16°, 5 7461 at 18° (Clarke's pecific Gravity Tables, new ed 32) V D 175 5, Mitscherlich (P 29, 193) Melts at 244° (Carnelley a Williams, C J 37, 127) Can be sublimed unchanged S 106 at 9°, 20-25 at 100° (Lassaugue) Very sal in alcohol and other Very sol in alcohol and ether (Lassugne)

HgBr Aq reddens litmus

Heated with phosphorus, Reactions -- 1 arsenic or antimony, forms bromide of P, As, or Sb - 2 Decomposed, yielding HgBr, by sunlight, or contact with copper or mercury, or by mixing with cuprous bromide dissolved in HBrAq -3 HgBr Aq with ammonia gives a white pp of HgBr NH₂ (Mitscherlich, J_pr 19, 455) - 4 HgBi NH, (Mitscherlich, J pr 19, 455) – 4 With sodium hypochlorite, HgBr Aq gives oxy chlorides xHgO yHgCl, (Rammel-berg) — 5 With hypochlorous acid, HgCl₂ and Hg(BrO₃), are formed (Balard) —6 Decomposed by nitric or sulphuric acid, giving off Br —7 Oxybromides, xHgO yHgBr, are obtained by boil ing HgBr Aq with mercuric oxide -8 Mixed with mercuric iodide and crystallised from ether or acetone, HgIBr is obtained, this compound is also formed by the action of an alkyl volide, eg LtI, on HgBr₂ dissolved in acetone (Oppen heim, B 2, 571) (v Mercury, wodobromide of, p 221)

Combinations -1 With hydrobromic acid to form bromomercuric acid HHgBr, (v infra) -2 Combines with many bromides of more positwo metals than Hg, to form salts regarded by Von Bonsdorff as bromomercurates (P 19, 839) These salts are obtained by evaporating solutions of the component bromides, the more important are HgBr, KBr and HgBr, 2KBr, HgBr, MgBr, and 2HgBr, MgBr, HgBr, SrBr, and 2HgBr, SrBr, (Löwig, P 14, 485) Salts containing NaBr, CaBr,, BaBr, and ZnBr, were also obtained by Von Bonsdorff (l.c.) Bromomercuric acid, HHgBr, was obtained by Neumann (M 10, 286), in long transparent needles, by slightly warming excess of HgBr. with HBrAq, filtering through asbestos, and sooling to between 0° and -4° . This acid is

readily decomposed by moisture or heat tion of HgBr2 in HBrAq reacts with alkalis to give HgBr₂ 2MX (M = alkali metal), the heat produced is c 27,200 for 2MOH, the solution of HgBr, in HBrAq probably contains the acid H.HgBr. -3 With mercuric cyanide and potascyanide, forms lustrous tablets of HgBr₂ HgCy₂ 2KCy 4H₂O (Geuther, A 29, 325) With mercuric cyanide and zinc cyanide, forms transparent prisms of HgBr₂ HgCy₂ ZnCy₂ 8H₂O (Varet, C R 109, 809) —4 Heated with mer curic sulphide, forms HgBr₂ 2HgS (Schneider, P 115, 167), this salt is also obtained by boiling HgBr₂Aq with freshly ppd HgS (H Rose, P 13, 59) (v Mercuric sulphide, Combinations, No 4, p 225)

Mercury, bromiodide of , v Mercury, wodo-

bromide of, p 221
Mercury, bromosulphide of, v Mercuric

sulphide, Combinations, No 4, p 225

Mercury, chlorides of Two chlorides are known, HgCl and HgCl₂ The molecular weight of the latter has been determined from the VD of the compound The numbers obtained for the VD of the former agreed with the formula HgCl, but it was shown that the vapour produced by heating mercurous chloride contained Hg and HgCl2, hence the V D could not decide between the possible formulæ HgCl and Hg2Cl2 More recently it has been found that the VD calculated from observations of VD of mer curous chloride vaporised into an atmosphere of HgCl₂ agrees with that required by HgCl (v infra)

MERCUROUS CHLORIDE HgCl (Protochlor-Calomel) Mol w very pro ide of mercury Sublimes at 400°-500° without bably 235 17 melting SG 6 993 (Karsten, S 65, 394), to 7 176 (Hassenfratz, A Ch 28, 3) VD 118 6 at 140° (Deville a Troost, C R 45, 821), 120 8 (Mitscherlich, P 29, 193) VD calculated for Odling showed that gold leaf is HgCl = 117.58amalgamated when exposed to calomel vapour at c 400° , hence he concluded that the vapour contained Hg, and that therefore the observed VD did not prove the formula HgCl (J 1864 Debray found that only a limited portion of the calomel vaporised at 440° is decomposed with separation of Hg (C R 83, 330), hence it appears impossible that calomel should have the molecular formula Hg_2Cl , else the observed V Dat c 440° would be considerably greater than 120 (calc for $Hg_1Cl_2 = 235 16$) In 1881, Fileti showed that when a mixture of mercurous and mercuric chlorides is heated to c 400° in a Pt tube, containing a tube of silver-gilt traversed by a stream of cold water, not a trace of Hg is deposited on the gilt tube He then determined the VD of a mixture of mercurous and mercuric chlorides, and calculated the VD of the mercurous chloride in the mixed vapours, the results were 115 9 and 120 1, hence the molecular formula of calomel is most probably HgCl (G 1881 341) S H at 7°-99°, 05205 (Regnault, A Ch [3] 1, 129) Crystallises in tetragonal forms, a c=1 17414 HF [Hg,Cl] = 32,600 (Thomsen, Z P C 2,21) For T C v. Von Lang, P 135, 29, for heat of vaporisation, w Marignac, C R 67, 877

Occurrence —As horn quicksilver, in tetra-gonal crystals. SG 6482.

Formation.—1 By passing Ol over excess of Hg; action proceeds slowly at ordinary temperatures, rapidly at near BP of Hg—2 By reducing HgCl,Aq, saturated at 50°, by SO₂ (Wohler, 4 90, 124, Sartorius, A 96, 325) —3 By reducing HgCl,Aq by oxalic acid in sunshine (Eder, 5 By ppg a mercurous salt by HClAq -6 By heating HgCl₂ with Hg -7 By heating HgSO₄ with Hg and NaCl -8 By triturating Hg with NaCl, Fe₂(SO₄)₃, and a little water, till the metal has lost its fluidity, and subliming

 $(Fe_2(SO_4)_3 + 6NaCl + 2Hg$ = $3Na_2SO_4 + 2FeCl_2 + 2HgCl)$ = Preparation —1 Anintimate mixture of 4 pts HgCl, with 3 pts Hg is made by moistening with alcohol and triturating until the Hg loses its fluidity, the mixture is gently heated for a few hours, again pulverised, and then slowly sublimed in a flask or retort, not more than a quarter filled with the mixture and placed on a thin layer of sand -2 4 pts Hg, 9 pts dry HgSO4, and 3 pts water are very intimately mixed, a quantity of NaCl equal to the weight of the Hg and HgSO, used is added, and the mixture is slowly heated till HgCl sublimes (Planche, A Ch 66, 168)-3 A well-pulverised mixture of 1 pt MnO₂, 1 pts NaCl, and 2 pts Hg is heated with 21 pts cone H2SO4, until HgCl sublimes 4 A warm dilute solution of HgNO, Aq, mixed with a little HNOs to prevent formation of basic salts, is ppd by excess of dilute NaClAq containing a little HCl, the liquid is heated for some time in contact with the pp which is then thoroughly washed with cold water in the dark (Scheele, of Frantwein, R P 11, 72, 12, 155, Mialle, J Ph 22, 586)—5 Cl is passed into HgNO, Aq, the pp of HgCl mixed with HgCl₂ is washed with hot water till HgCl₂ is all dis solved, the HgCl is then crystallised from warm HgNO, Aq (Sievers, B 21, 647)

Properties - White, semi transparent, tetragonal, prisms, if sublimed quickly, forms a fibrous mass of small crystals When powdered, calomel shows a slight lemon yellow colour Highly refractive and dispersive Tasteless and inodorous Sublimes without melting qute insol water, alcohol, ether, and dilute acids Sl sol cold, more sol hot, HgNO₂Aq (v Debray, O R 70, 995, cf Drechsel, J pr [2] 24, 44) Boiled with HClAq, HgCl₂ goes into solution, and Hg is separated, with conc hot H₂SO₄, HgCl₂ and HgSO₄ are formed HgCl 18 decomposed by solutions of alkalis, alkaline earths, and alkaline carbonates, with ppn of Hg₂O For experiments on V D of calomel, v

Reactions —1 Exposed to sunlight, HgCl darkens with separation of Hg (for action of heat on HgCl v supra) -2 Partly decomposed by aqueous vapour or boiling water, with production of HgCl₂ and Hg —3 Decomposed by many metals when heated with them in presence or absence of water, giving metallic chlorides and Hg —4 Triturated with wodine and water, HgCl₂ and HgL are produced (Planche a Soubeiran, J Ph 12, 651)—5 Heated with a little sulphur, HgS and HgCl, are formed, with excess of S, the products are HgS and S,Cl. -6 Heated in phosphorus vapour, HgCl yields PCl, and Hg phosphite (Davy).—7. By heating an intimate

mixture of 3 pts HgCl with 1 pt arsenic, a sub limate is obtained consisting in part of yellow tetrahedral crystals, according to Capitaine (J pr 18, 422) these crystals are mercuri-arsenic chloride AsHgCl The compound is decomposed by hot water to As Hg amalgam, As2O3 and HCl, it is partly decomposed by heat, giving Hg, As, and AsCl₃-8 Reduced by sulphurous acid, also by hot stannous chloride solu tion, with separation of Hg - 9 Cold sulphuric acid has no action on HgCl, the hot cone acid forms HgCl₂, HgSO₄, and SO -10 Dissolved by hot nitric acid with evolution of NO, the solution contains Hg(NO₂)₂ and HgCl₂ -11 Boiling hydrochloric acid forms HgCl₂ and Hg, boiled in an open vessel with water and a little HCl, no Hg is separated, but HgCl, goes into solution -12 Decomposed by hydrocyanic acid solution, forming HgCy, Hg, and HCl -13 With solution of alkali chlorides forms HgCl, which combines with the excess of alkali chloride to form double salts, some of which are soluble and some insoluble -14 Digested with solutions of alkalı vodides, or vodide of magnesium, or won, HgI is separated, and metallic chloride goes into solution -15 Solutions of alkalis form Hg2O and alkalı chloride, heated with solid alkalıs, Hg, O, and alkalı chloride are produced -16 Ammonia produces black NH Ilg Cl (v MFRCURAMMONIUM COMPOUNDS) —17 Heated with carbonates of calcium, barrim, or magnesium, Hg, Hg,O, and HgO are separated, and CO is evolved (Buchner, R P 3, 31, 4, 289, Vogel, R P [3] 1, 34) -18 With alkali sulphites in solution, Hg separates, and a double sulphite of Hg and alkali metal goes into solution 19 Rubbed with antimony tri or penta sul phide, HgS and SbCl, are formed

Testing calomel for impurities -HgCl some times contains HgCl₂, HgNO₃, or Hg(NO₃), or Hg HgCl₂ is detected by shaking with water, filtering, and adding SnCl.Aq, when a white grey pp is produced Bonnewyn (Bl [2] 4, 201) says that 1 pt of HgCl in HgCl may be detected by immersing a clean knife blade in the calomel moistened with alcohol or ether, if HgCl, is present a black spot is formed on the blade HgNO₃ or Hg(NO₃)₂ is detected by heating, when NO₂ is evolved Hg may be detected by examination under the microscope HgCl may be adulterated with powdered heavy spar, &c , this remains unchanged on sublima tion Adulteration with gum or other organic material is detected by the smell produced on

heating

Combinations -1 With sulphur chloride, to form 2HgCl SCl2, produced by long continued warming HgCl with S2Cl2, also by heating an intimate mixture of 31 pts HgCl₂ and 2 pts S in a dish covered with a funnel, on to which the double compound sublimes, also by heating As2S, with HgCl2

(7HgCl₂ + As₂S₃ = 2AsCl₃ + 3HgS + 2Hg₂SCl₄)Forms rectangular needles, which melt to a brown liquid, and volatilise without decomposi tion, decomposed by water (Capitaine, J pr. 18, 422) —2 With stannous chloride to form 2HgCl SnCl. Produced by heating an amal gam of 8 pts Sn with 1 pt Hg mixed with 24 pts HgCl, and subliming Forms white dendritic crystals, partially decomposed by heat;

Coefficient

wholly decomposed by water, with formation of SnCl₂ which reduces the HgCl (Capitaine, J pr 18, 422) —3 H Rose (P 44, 325) states that

HgCl combines with sulphur dioxide

Mercurio chloride HgCl₂ (Perchloride of
mercury Corrosive sublimate) Mol w 270 54 [288°] (Carnelley, C J 33, 276) (303°) (Carnelley a Williams, C J 33, 282) S G 6 223 (Playfair a Joule, C S Mem 2, 401), 5 448 (Schroder, P 107, 113) V D 136 3 (Mitscherlich, P 29, 193) S H 12°-45° 064 (Kopp, Tr 155, 71), 138 088 (1890 (Parment) A Ch (131, 139) 13°-98° 06889 (Regnault, A Ch [3] 1, 129) S 5 78 at 0°, 6 57 at 10°, 7 39 at 20°, 8 43 at 30°, 9 62 at 40°, 11 34 at 50°, 13 86 at 60°, 17 29 at 70°, 24 32 at 80°, 37 05 at 90°, 53 96 at 100° (Poggiale, A Ch [3] 8, 463) S cold alcohol 43 5, boiling alcohol 86 2, S ether 33, S glycerin 7 (Fairley, M S [3] 9, 685) Crystallises in two forms belonging to the trimetric system (1) crystals from alcoholic solution, abc = 7254 1 1 0686, (11) crystals by sublimation, a b c = 9347 1 3396(v Mitscherlich, P 28, 118, Von Lang, W A B 45, 119) H F Z P C 2, 21) $[Hg,Cl^2] = 54,490$ (Thomsen,

Occurrence - In a volcanic district on Ternate, one of the Molucca islands (Frenzel, Min

Mittheil 1877 305)

Formation 1 By heating Hg in excess of Cl 2 By dissolving HgO in hot HClAq, and evapor ating 3 By dissolving Hg in hot HClAq con taining some HNO, evaporating, and recrystal lising from hot water -4 By adding excess of Cl to a slightly acid solution of Hg(NO₃) (Sievers, B 21, 617)

Preparation - 1An intimate mixture of equal parts NaCl and HgSO, (obtained by boiling 4 pts Hg with 5 pts cone H SO, till a dry mass is formed), to which a little MnO, has been added (to prevent formation of HgCl from Hg,SO, which may be present), is slowly heated in a long necked flask or retort, HgCl, sublimes on the cooler parts of the apparatus The operation must be conducted in a good draught cupboard because of the very poisonous nature of $HgCl_2$ —2 Boiling cone $HgNO_3Aq$ is mixed with cone HClAq as long as a μp forms, the pp of HgCl is boiled with as much HClAq as was used in its formation $(HgNO_1Aq + 2HCl = HgCl_2Aq + H_1O + NO_2)$, crystals of $HgCl_2$ separate on cooling, they may be recrystallised from hot water

Properties -Translucent crystals, forming a white powder when crushed HgCl2 has a dis agreeable metallic taste, it is extremely poison ous Melts at 288° (v supra) to a colourless liquid; according to Haass, HgCl, does not melt when horted if the pressure is less than 120 mm (B 13, 2203) Easily sol water, sol alcohol, ether, and glycerin (v supra) Schröder (J R 1886 18) gives the following table, showing the S G of aqueous and alcoholic solutions of HgBl, and the percentage of HgCl, in these solutions

Aqueous solutions of HgCl.

P.c. HgCl. 8G compared with water 309 1 00836 1 22 101008 1 0099 1 00575 2 434 1 02035 1 02018 1 01856 1 01585 8 578 1 0305 1 03022 1 02855 1 02577 4-725 1.0407 1.04038 1.03856 1 03566

Alcoholic solutions.

_		_			over.creme
P.e			withwate	rat 4°	of change
HgCl,	00	-10°	20°	300	of SG
0	8315	82286	81435	80594	000849
1 22	8397	8312	8228	·8141	000854
2 38	8484	8399	8314	8227	000858
4 42	8635	8549	8403	8375	000867
8 56	8966	8877	8789	8698	000891
243	9308	9213	9119	9024	000946
1591	9620	9523	9125	9329	000971
$19\ 32$	9951	9852	9753	9652	000997
22 46	1 0285	1 0184	10083	9982	001013

HgCl Aq reacts slightly acid to litmus boiling HgCl2Aq some HgCl2 passes off with the HgCl2Aq is decomposed by light with evolution of O and formation of HCl and Hg
oxychloride (cf V Meyer, B 20, 2970)
Reactions —1 Many metals decompose HgCl,

when heated with it, forming HgCl or Hg, such metals are Sb, As, Bi, Cu, Fe, Pb, Ni, Sn Many metals also reduce HgCl₂ in aqueous solution, generally ppg HgCl and Hg, Cd, Fe, and Zn pp Hg only -2 Reducing agents, e.g. SnCl₂Aq, 50 Aq, formic acid, oxalic acid, produce HgCl (cf 1 der, B 13, 166, also Wurt's Dictionnaire, Suppl p 1066) -3 With many carbon com punds, HgCl, forms HgCl and HCl (the H being withdrawn from the C compound) -4 HgCl2 is not decomposed by sulphuric or nitric acid, it dissolves fairly easily in HNO3Aq -5 Dissolves in hot cone hydrochloric acid, on cooling, a white crystalline mass is obtained which has the composition 2HgCl HCl according to Boullay (A Ch 34, 243, cf Combinations, No 1) -6 Ac cording to Fairley (B A 1875 42), hypochlorites reduce HgCl2 to HgCl -7 Albumen is lapidly coagulated and ppd by HgCl Aq, white of egg serves as an antidote to poisoning by corrosive sublimate -8 Boiled with mercuric oxule, oxychlorides are obtained (v MERCURY, OXYCHIORIDES or, p 223) - 9 Alhalis produce HgO and alkalı chloride—10 Normal potassium or sodium carbonate ppts HgO, K(or Na)HCO, is also formed, and this reacts with the rest of the HgCl, to pp oxychlorides -11 Potassium (or sodium) hydrogen carbonate produces various oxychlorides (q v p 223) -12 Phosphorus trihydride produces a black pp when passed into HgCl, dissolved in water or alcohol, on con tinuing the passage of PH₃, the pp becomes yellow, and then has the composition P,Hg, 3HgCl₂3H₂O = 2(PHg₂Cl HgCl₂)3H₂O, the solution contains HCl This compound is known dimercuri phosphonium mercuric chloride, it must be washed quickly with cold water, and dried over H2SO, in vacuo, it is de composed by hot water, giving Hg, HCl, and R₁PO₃, heat produces HCl, Hg, and H₃PO₄ (H Rose, P 40, 75) —13 Arsenic trihydride produces a brown yellow pp in HgCl₂Aq This pp has the composition AsHg₂Cl HgCl₂, it is known as dimercuriarsonium-mercuric chloride The pp is washed with cold water and quickly dried over H₂SO₄ in vacuo, it is decomposed by water to Hg, As₂O₃, and HCl (H Rose, P 51, 123)

Combinations -1 With hydrochloric acid. according to Boullay (A Ch 34, 243) the compound 2HgCl, HCl is obtained by dissolving HgCl, in hot cone. HClAq, and cooling, this compound forms a crystalline lustrous mass which melts by the heat of the hand (v also Ditte, O. R. 92, 853) Neumann (M 10, 236) obtained chloromercuric acid HHgCl₂ by gently warming excess of HgCl2 with HClAq, filtering through asbestos, and cooling to between 0° and -4° This acid is very readily decomposed by heat or moisture Solutions of HgCl in HClAq react with alkalis to form HgCl, 2MX (M = alkalı metal), the heat produced in the reaction is c 27,200 for 2MOH, the solution of HgCl2 in HClAq probably contains the acid H.HgCl. Dry HCl passed over well-cooled $HgCl_2$ has no action (N, lc) —2 With many chlorides and with some other salts The chief compounds with other chlorides are the following (v Von Bonsdorff, P 17, 115) -

(1) With phosphorus pentachloride 3HgCl₂ 2PCl₅ Pearl white needles, sublimes unchanged, decomposed by water, formed by heating the constituents together (Baudrimont,

A Ch [4] 2, 45)
(11) With alkalı chlorides (a) chloride2KCl HgCl, H,O, potassium KCl HgCl₂ H₂O, KCl 2HgCl₂ 2H₂O The first salt is formed by saturating KClAq with HgCl₂ at 30°, adding as much KCl as originally used, and evaporating The second salt is produced by evaporating a solution of equal equivalents of KCl and HgCl₂ (Rammelsberg, P 90, 34) The third salt results by saturating KClAq at 60° with HgCl₂ and allowing to cool The com 60° with HgCl, and allowing to cool pound 6KCl 3HgCl, CuCl, 2H,O was obtained by Von Bonsdorff (P 33, 81) by adding CuCl, 2Aq to a dilute solution of KCl HgCl₂ (b) With sodium chloride 2(NaCl HgCl₂) 3H₂O, 2NaCl HgCl, The first salt is obtained by adding NaCl to NaClAq saturated with HgCl2. The second salt is produced by adding alcohol to saturated NaClAq shaken with powdered $HgCl_2$ (c) With rubidium chloride 2RbCl HgCl₂, RbCl 2HgCl₂, RbCl HgCl₂ Ob tained, respectively, by evaporating a neutral solution of RbCl and HgCl, by evaporating a solution of equal parts of the constituent salts, and by heating the second salt to 50 (Godeffroy, Ar Ph [3] 12, 47) (d) With ammonium chloride 2NH,Cl HgCl₂H₂O (sal alembroth) is obtained by evaporating a solution of 1 pt NH,Cl and 2 pts HgCl2, loses H2O in dry air, isomorphous with the corresponding K salt The other salts obtained are NH, Cl HgCl, 2NH₄Cl 2HgCl₂ 2H₂O (Kane), 2NH₄Cl 9HgCl₂ and 2NH, Cl 3HgCl, 4H,O (Holmes, C N 5,

(iii) With alkaline earth chlorides (a) With calcium chloride CaCl25HgCl28H2O, by saturating warm CaCl2Aq with HgCl2, and cooling, by evaporating the mother liquor the salt CaCl₂ 2HgCl₂ 6H₂O is obtained strontium chloride SrCl, 2HgCl, 2H,O (c) With barium chloride

BaCl₂ 2HgCl₂ 2H₂O (d) With michloride MgCl₂ 3HgCl₂ 5H₂O and (d) With magnesium

MgCl₂ HgCl₂.6H₂O

(1V) With chloride of zinc ZnCl, HgCl, 4H,O, by evaporating a mixed solution of the constituents. Analogous salts with CuCl, CoCl, NiCl, and FeCl, have been obtained

The chief compounds with oxysalts are

the following .-

(1) With ammonium sulphite $3 HgCl_2 2(NH_4)_2SO_3$ By adding hot saturated $HgCl_2Aq$ to cold $(NH_4)_2SO_3Aq$ (P de Saint-Gilles, A 84, 266, 269)

(11) With potassium chromate, and dichrom ate (a) HgCl₂ K₂Cr₂O₇, by cooling a warm solution of equivalents of the two salts (Millon, A Ch [3] 18, 388, Darby, C S Mem 1, 24) (b) 2HgCl₂ K₂CrO₄, by mixing solutions of the constituent salts in the ratio 2HgCl, K,CrO, adding HClAq sufficient to dissolve ppd HgCrO. and evaporating (Darby, lc)

(111) With ammonium dichromate (a) HgCl₂ (NH₄)₂Cr₂O₇ H₂O, by evaporating a solution of the constituents (Abel a Richmond, C J 3, 202, cf Darby, C S Mem 1, 24, Zepharo vich, W A B 39, 17) (b) HgCl, 3(NH,), Cr,O,, by evaporating the mother liquor from the first salt (A a R, Lc; of Clarke a Stern, Am. Ch 3, 351)

(1v) With copper acetate

 $2HgCl_2Cu(C_2H_3O_2)_2CuO$, deposited from a mix ture of cold saturated solutions of HgCl, and $Cu(C_2H_3O)_2$ (Hutteroth a Wöhler, A 53, 142)

(v) With chlorochromtetrammonium chloride 6HgCl, Cl2Cr28NH3 Cl4, by spontaneous evaporation of a mixed solution of the two salts (Cleve,

J 1862 150)

3 Compounds of HgCl2 with PHg Cl and AsHg,Cl areknown (a) Dimercuriphosphonium mercuric chlorule 2(PHg2Cl HgCl) 3H O, ayellow solid formed by passing PH, into HgCl, dissolved in water or alcohol (v Reactions, No 12) Dimercuriarsonium - mercuric chloride AsHg₂Cl HgCl₂, a brown yellow pp by passing AsH₃ into HgCl₂Aq (v Reactions, No 13) -4 A compound of HgCl2 with mercuric sulphocyanide - HgCl₂ Hg(CSN)₂—is obtained by the reaction of SOCI, with Hg(SCN), (McMurtroy, C J 55,

Mercury, chlorocyanide of, v Mercury, cyanochloride of, infra

Mercury, chlorosulphides of, v Mercuric

sulphide, Combinations, No 4, p 225 Mercury, chloro-iodides of, v Mercury, wolochlorides of, p 221

Mercury, chromates of, v vol 11 p 155 Mercury, cyanides of, v vol 11 p 312

Mercury, cyanochloride of HaCyCl Quadratic prisms, stable in air, produced by evaporating an aqueous solution of equivalent weights of $HgCl_{2}$ and $HgCy_{2}$ (Liebig, S 49, 253, Poggiale, C R 23, 762, cf Weeren, J pr 64, 63)

Mercury, cyanoselenides and cyanosulphides of, v Mercury, selenocyanides and sulpho cyanides of, under Cyanides, vol 11 pp 348 and

Mercury, ferrocyanides of, v vol 11 p 335 Mercury, fluorides of Two are known, HgF and HgF₂, the VD of neither has been determined. These fluorides are remarkably unstable both as regards the action of water and of heat

MERCUROUS FLUORIDE HgF or Hg2F2 pared by adding freshly ppd Hg₂CO₂ to HFAq so long as the salt is dissolved, and evaporating, also by adding recently prepared HgCl to a solution of Ag.CO, in HFAq, filtering from AgCl, and evaporating on a steam bath (Finkener, A 110, 142) Berzelius obtained HgF, mixed with HgCl. by subliming a mixture of HgCl with NaF HgF is a light yellow, crystal me, powder It is partly dissolved, and partly decomposed to HF and Hg₂O, by water Exposed to light when moist it is blackened HgF may be heated to c 200° without change, above this temperature Hg sublimes and the glass vessel is corroded HgF is decomposed by alkalis with separation of Hg₂O, the action of NH₃Aq is more complex HgF absorbs NH₃ gas forming N₂H₆Hg₅F₂ (v Mercurammonium compounds, p 206) Combines with SiF, to form Mercurbus silicofluoride Hg₂SiF₆ 2H₂O (v Mercury, silicofluorides of, p 224)

MÉRCURIO FLUORÌDE HgF₂ According to Fremy (A Ch [3] 47, 5), crystals of this com pound are obtained by dissolving HgO in excess of Hi Aq, and evaporating the solution slowly over lime Finkener (P 110, 628) obtained an oxyfluoride, HgF₂ HgO H₂O, by this method, by adding cone HFAq (50 p c) to this oxyfluoride, it was suddenly changed to a white crystalline mass of HgF₂ 2H₂O (Finkener, Lc) The hy drated fluoride is decomposed at 30°, giving H₂O, HF, and HgO HgF₂ H₂O (F) HgF₂ is decomposed by water with separation of HgO Addition of slight excess of NH₃Aq to HgF₁ in HFAq ppts NH₂Hg₂OF HF (Finkener, P 110, 632) Mercuric silveofluoride HgSiF₆ 6H₂O probably exists (v Mercury, silveofluorides of, p 224) Berzchus obtained a compound of HgF₂ with NH₄F by treating HgF₂ with NH₄Aq HgF₂ combines with HgS (v Mercuric sulphide, Combinations, No 6, p 225)

Mercury, fluosulphide of, v. Mercuric sul-

phide, Combinations, No 6, p 225.

Mercury, fulminate of, v vol 11 p 317 Mercury, haloid compounds of Two series of these compounds exist, HgX and HgX, molecular weights of HgCl, HbBr, and HgI, are known, the molecular weights of HgCl, HgBr, and HgI are probably as represented by these formulæ The compound HgI HgI also exists, and a periodide of Hg has been isolated mercurous compounds Hgl are insoluble in water, except Hgl, which is partly dissolved, and partly decomposed, by water, the mercuric com pounds Hgl, are soluble in water, with the ex ception of HgF2, which is decomposed by water The Hg haloid compounds combine with many other haloid compounds, and also with oxysalts, to form numerous double salts The double salts of the type HgX2 M1X and HgX2 2M1X are best regarded as salts of the mercur halogen acids HIIgX, and H HgX, respectively, the acids HilgX, have been isolated, and probably also the acids H.HgX, The heats of formation of HgX and HgX₂ decrease as the atomic weight of X increases Thomsen gives the following data (Z P C 2, 21) X [Hg,X

An iodochloride HgICl, and an iodobromide

HgIBr, have been isolated

Mercury, hydrated oxide of According to Carnelley a Walker (C J 53, 80), the hydrate HgO H₂O is obtained by ppg HgCl₂Aq by NaOHAq, and drying in air, it is stable to about 100°, and is completely dehydrated at c 175° According to Schaffner (A 51, 181) the yellow pp formed by adding KOHAq to solution of a

mercuric salt is HgO 3H₂O (v Mercuric oxide, p 222) But according to Millon (B J 27, 112), Marchand (J pr 37, 277), Rammelsberg (J pr [2] 38, 559), and Wallace (Chem Gazette, 1858 345), the pp obtained from Hg salts by KOHAq is HgO

Mercury, lodides of Besides the lodides HgI and HgI₂, corresponding with the chlorides, bromides, and fluorides, of Hg, there is said to exist a definite mercuro increuric lodide, HgI HgI₂, and a hexa lodide HgI₃. Hg and I combine directly with production of heat

HgI HgI₂, and a hexa iodide HgI₄. Hg and I combine directly with production of heat Mercurous former HgI or HgI₂. Mol w not known with certainty Melts at c 290° (with partial decomposition according to Stroman, B 20, 2818) Boils at c 310° with partial decomposition (Yvon, C R 76, 1607) S G 775 (Boullay, A Ch [2] 43, 206) S H 17°-99° 03949 (Regnault, A Ch [3] 1, 129) Crystallises in tetragonal forms, a c = I 1 6726 (Des Cloizeaux, C R 84, 1418) H F [Hg,I] = 15,550 (Thomsen, Z P C 2, 21)

Formation —1 By subbing together Hg and I, in the ratio Hg I, moistened with a few drops of alcohol, and removing the small quantity of HgI, which is always formed by treatment with alcohol, in which HgI. is soluble but HgI is in soluble —2 By rubbing together HgI and Hg in the ratio HgI Hg, and dissolving out unchanged HgI by alcohol—3 By heating 10 parts I with 10½ parts Hg in a retoit, on a sand bath, to not above 200°, HgI sublines in red crystals, be coming yellow when cold (Yvon, C R 76, 1607) 4 By adding KIAq to solution of a mercuric salt, preferably the acetate (v Lefort, Ph [3] 3, 823)

Preparation—A cone solution of HgNO, containing a little HNO, and free from basio mitiate, is heated to boiling with excess of I, when the I is partially dissolved the liquid is carefully decented into a warm basin, on cooling, very lustrous transparent, yellow tablets of HgI separate. The crystals are brought on to a filter (best in the dark), washed with cold water containing a little HNO,, and then with pure cold water, and dried in the dark at ordinary summer temperature by placing them on filter paper which is frequently changed (Stroman, B 20, 2819). HgI is obtained as a flocculent pp by rapidly adding a fairly cone solution of I in alcohol to cold cone HgNO, Aq (S, Ic)

Properties and Reactions -HgI crystallises in yellow tetragonal tablets, isomorphous with HgCl HgI is sometimes described as a green powder Stroman (lc) says that green preparations are impure When heated, the yellow orystals become dark yellow, then orange, and finally garnet red Yvon $(C \ R \ 76, 1607)$ says that the change of colour begins at 70°, and assigns a definite temperature for each change of colour Stroman (B 20, 2818) could not connect the different colours with definite intervals of temperature, he says that the salt prepared by him was pure yellow at 100° Sublimation be gins at c 190° according to Yvon, at c 110°-120° HgI when moist is according to Stroman rapidly blackened by light HgI is very slightly soluble in water, insoluble in alcohol. It is easily decomposed to Hg and HgI_2 , \mathfrak{sg} by HIAq , KIAq , and $\mathrm{similar}$ includes. Heated rapidly HgI gives a sublimate of Hg and HgI HgI, HgI is used in medicine For medicinal purposes it must be quite free from HgI2, which is a violent poison.

MERCURO MERCURIO IODIDE HgI HgI2 compound of Hg and I of this composition was obtained by Boullay (A Ch [2] 34, 845) by adding KIAq containing I, in the ratio KI 1, to HgNO, Aq The same compound is said to be obtained by adding KIAq to HgNO, Aq and digesting the pp for some time in the liquid, also by rubbing together HgI, and I in the ratio 3HgI2 Hg Mercuro mercuric iodide is described as a yellow powder, insol water and alcohol, unchanged in the dark, but becoming dark when exposed to light When heated, it turns red, then melts, and may be sublimed unchanged, yielding crystals which are red when hot but become yellow on cooling HIAq, and various iodides in solution, dissolve HgI₂ leaving HgI, and then decompose the HgI with separation of

MERCURIC TODDE HgI_2 Mol w 452 86 [238°] (Carnelley a Williams, C J 33, 283) (339°-359°) (C a W, l c) S G red variety 6 2941 to 6 3004 at 0°, 6 276 at 126°, yellow variety 6 225 at 126° (Rodwell a Elder, Pr 28, 284), 6 179 at 200° solid, 5 286 at 200° molten (R a E, le). VD 2257 to 2344 (Mitscherlich, P 29, 193) SH 18°-99° 04197 (Regnault, A Ch [3] 1, 129) Crystallises in tetragonal forms (red), ac=1 1 9055, also in rhombic forms (yellow), $pp=114^{\circ}$ 30' H F [Hg,I']=25,640 (Thomsen, Z P C 2, 21) Change of yellow to red crystals is accompanied by production of heat, 3000 gram units (Berthelot, Bl [2] 39, 17, cf Weber, P 100, 127) S 004 at 17 5°, 005 at 22°, S 286 50 pc alcohol at 18°, 1 186 absolute alcohol at 18° (Bourgoin, Bl [2] 42,620)

Formation —1 By the action of I on Hg, Dublanc (Ph C 1849 656) says that pure HgI, is obtained by pouring 1,000 pts alcohol (93 p c) on to 100 pts Hg, and adding 124 pts I in por tions of 10 pts at a time, after each addition of I, the whole is agitated until the alcohol becomes colourless, the addition of the last portion of I should leave the alcohol coloured, the HgI2 13 washed with alcohol -2 By adding KIAq or

FeI2Aq to HgCl2Aq

Preparation —1 8 pts HgCl₂ and 10 pts KI are dissolved, separately, in water, the solutions are mixed, and the pp is thoroughly washed with cold water Any excess of KI dis solves some HgI2, and any excess of HgCl2 pro duces a yellowish pp containing more or less HgCl₂ Williams (Ph [3] 3, 1015) dissolves 8 pts HgCl₂ in 4 pts NH₄Cl in water, and then adds 10 pts KI in water -2 10 pts I are sus pended in water, and Fe filings are added until all the I is changed to FeI, the solution is at once added to a solution of 10? pts HgCl₂ in water, the pp of HgI, is rapidly separated from the liquid (to prevent formation of Fe oxychlor ides) and washed with cold water By crystal lising from hot KIAq, or, better, from hot cone HClAq (Köhler, B 12, 608), HgI, is obtained in very lustrous, red tetragonal prisms, with a greenish reflection

Properties - HgI, obtained by ppn is a pure scarlet coloured, crystalline, heavy powder is sl sol. water, S = 66 (Wurtz) Sol hot alcohol; somewhat sol glycerin (in 340 pts , Fairley,

M. S [3] 9, 685); also in ether, and some oils. Sol KlAq, also in cone hot HClAq, from these solutions HgI₂ separates in well formed crystals HgI₂ is dimorphous Red (tetragonal) HgI₂ is changed to the yellow (rhombic) modification by heat, the change occurs at 126° (Rodwell a Elder, Pr 28, 284), it is accompanied by a sudden, and then by a regular, expansion SG red at 126° = 6 276, yellow at 126° = 6 225 (R a E) HgI, melts at 238° (Carnelley a Williams, C J 33, 283), at 253°-254° according to Kohler (B 12, 608), to a blood red, liquid, melting is attended with considerable expansion At c 339°-359° the liquid boils, and sublimes to yellow rhombic plates The yellow variety passes into the red at the ordinary temperature, this change is hastened by rubbing or scratching the red crystals, heat is produced in the process, 3,000 gram units according to Berthelot (cf Weber, P 100, 127) The HgI₂ obtained by adding cold KIAq to cold HgCl Aq appears at first yellow, but it quickly changes to red, the change of crystalline form in this case may be observed under the microscope Solutions of HgI₂ in alcohol, ether, or KIAq are colourless, if the HgI2 is allowed to form slowly from these solutions, the crystals are red, but if the ppn is made rapid, e g by pouring an alcoholic solu tion into water, the crystals appear yellow for a moment, but they quickly change to red (cf Schiff, A 111, 371, Selmi, J 1855 417)

Reactions—1 HgI₂ dissolves in hydrodic

acid solution with production of heat (v Bei thelot, Bl 38, 369) This solution has about the same heat of neutralisation as HIAq (Thom sen), with alkalis it forms salts HgI, 2MI, the solution very probably contains the acid H2HgI, (cf Combinations, No 2) An iodomercuric acid, HHgI₃, has been obtained by slightly warming excess of HgI, with HIAq, filtering through asbestos, and cooling to between 0° and -4° (Neumann, M 10, 236), this acid is very readily decomposed by moisture and by heat According to Boullay (A Ch [2] 34, 345) a solu tion of HgI₂ in hot HIAq deposits I on cooling, and then crystals of 2HgI₂ 3HI —2 Most heavy metals, eg Zn, Sn, when triturated with HgI, remove I and leave Hg, potassium acts in the same way -3 HgI Aq is decomposed by alkalis, with separation of HgO and formation in solu tion of a double salt xHgI, yMI Baryta and strontia react similarly to alkalis -4 Lime, sodium carbonate, and potassium carbonate do not decompose HgI,Aq, but a solution of HgI, in alcohol is decomposed by these reagents -5 HgI, dissolves in hot calcium hypochlorite solution, on cooling Ca periodate is deposited and HgCl, remains in solution (Rammelsberg) 6 When HgI₂ is boiled with nitric acid, S G 15-14, Hg(IO₃)₂ is formed, with acid S G 13, white leaflets of HgI₂ Hg(NO₃)₂ separate, with acid S G 12, crystals of unchanged HgI₂ are obtained, together with some of the compound HgI, Hg(NO3)2 (Kraut, 7 18, 3461) -7 Chlorine, passed into water containing HgI, in suspension, produces a yellow solution containing HgCl2 and ICl₃ (Filhol)

Combinations -1 With hydriodic acid (v Reactions, No 1) -2 With various metallic iodides to form double salts, regarded by Von Bonsdorff as iodomercurates (P. 17, 265). These salts have been examined chiefly by Boullay (A Ch [2] 34, 345) They are generally obtained by dissolving HgI, in a solution of the other rodide and evaporating The fol

lowing are the most important

(1) With alkali rodides (a) With potassium rodide 2HgI, 2KI 3H, 0, HgI, 2KI The former is produced by saturating boiling KIAq with HgI₂, filtering, separating from HgI₂ which crystallises out, and evaporating Sol alcohol and ether Decomposed by water, with forma tion of HgI₂, and HgI₂ 2KI which separates on evaporation Thes, soluble salts may be pre pared by boiling KIAq with HgO, the solution contains the double salts and also KOH (cf Jehn, Ar Ph [3] 1, 97) (b) With sodium wodide NaIAq reacts with H₆I₂ similarly to KIAq, the compositions of the double salts of NaI with HgI₂ have not been satisfactorily de (c) With ammonium rodide termined 2(NH₄I HgI₂) 3H₂O, obtained, as yellow needles, by dissolving HgI2 in hot NH, IAq, separating from HgI, which forms on cooling, and evapora

(11) With other metallic rodides Bal, Srl, CaI2, and MgI2 solutions react with HgI2 simi larly to kIAq, the double salts are probably MI₂HgI₂ HgI₄ appears to form double compounds with CdI₄ and FeI₄. The compound $2 \mathrm{HgI}_2 \,\mathrm{Cu}_2 \mathrm{I}_2$ was obtained by Hess (D P J 218, 183) -3 HgL combines with mercuric chloride, also with mercuric bromide (v. Mercury, iodo chlorides and iodobromide of, infra) —4. Com bines with mercuric sulphide (v sulphide, Combinations, No 5, p 225) Mercuric

This per-MERCURY, HEXA IODIDE OF Hgl. nodide is said by Jörgensen (J pr [2] 2, 357) to be obtained by adding cold HgCl,Aq, followed by addition of water, to an alcoholic solution of KI, heated to 50° If the solutions are mixed hot, large rhombic crystals of HgI, are formed, but they are always mixed with HgI₂ HgI₈ is decomposed quickly by alcohol, slowly by water, with formation of red HgI2 HgI, possesses most of the optical properties of tourmalin

Mercury, iodobromide of HgIBr Sulphur yellow, translucent, rhombic prisms, a b c = 6443 1 9194 (Groth, B 2, $5\overline{7}4$) Melts at c 229° , and boils at c 360° , crystallisable from ether, may be sublimed unchanged Produced by crystallising a mixture of HgI2 and HgBr2 from ether or acetone, also by the reaction of an alkyl iodide, eg EtI, on HgBr, dissolved in

acetone (Oppenheim, B 2, 571

Mercury, iodochlorides of Two iodochlorides (1) HgL 2HgCl2 of Hg have been isolated $= Hg_3L_2Cl_4$ Obtained by dissolving HgI, in hot HgCl, and cooling (Liebig, S 49, 252), also by boiling HgCl with excess of I and much water until I vapour is no longer given off (Selmi, J 1855 417) (11) HgIČl Prepared by heating, in a closed tube at 140°-160°, HgI, HgCl, and a little water, until no HgI, remains unchanged (Köhler, B 12, 1187) Boullay (P 48, 175) said that HgICl is produced by satura ting hot HgCl₂Aq with HgI₂, but Köhler found that very little was formed in this way HgICl forms a citron-yellow crystalline mass, which becomes red after about 12 hours. The red modification forms tetragonal, the yellow forms rhombic, crystals. HgICl is citron-yellow at

c 125°, it melts at c 158° to a golden coloured liquid which solidifies at c 146°, it is slightly soluble, with partial decomposition, in hot water, more soluble in alcohol HgICl may be sublimed, with only slight decomposition, in a stream of HCl, SO2, or H2S From a solution of HgICl in dilute HClAq, H2S ppts a yellow solid, probably HgICl HgS (Kohler, lc)

Mercury, 10dosulphides of, v Mercuric

sulphide, Combinations, No 5, p 225
Mercury, nitride of Hg, N₂ (Trimercur amine) This compound was first isolated by Plantamour (A 40, 115) Ppd HgO is dried at 40°-50°, and then heated at 100° in a stream of dry NH_2 so long as water is evolved (Hirzel, J1852 419) Plantamour directed to pass NH, over cold HgO, then to heat to 150° in NH,, and finally to remove unchanged HgO by HNO, Aq, Hirzel found that HNO, Aq reacts with Hg, N, Mercury nitride is a brown powder, very explosive, but requires a higher temperature, or a stronger blow, than nitrogen iodide to explode it Hg₃N₂ is not acted on by cold dilute H SO, Aq, the hot acid decomposes it Conc H.SO, reacts energetically and explosively Conc HNO, Aq forms Hg(NO,), and NH, NO, dilute HNO, Aq forms a white powder, HClAq forms HgCl2 and NH,Cl Mixed with KOH and heated, NH, and Hg are formed Moist Hg, N, is slowly decomposed by light, in water it is

changed, after 24 hours, to a white powder
Mercury, oxides of Two oxides of Hg are
known, Hg₂O and HgO, it is doubtful whether Hg₂O has been obtained free from Hg and HgO Neither oxide has been gasified, and the mol w

of neither is known with certainty

MERCUROUS OXIDE Hg.O (Suboxude, or black oxude, of mercury) This oxide is prepared by adding NaOHAq or KOHAq to solution of a mercurous salt, or to HgCl suspended in water The best salt to use seems to be HgNO, it should be dissolved in water with a very little HNO, the solution being made dilute, ppn with KOHAq, and washing with cold water, should be performed in the dark, and the black pp should be dried in the dark without heating Guibourt (A Ch [2] 1, 422) says that Hg₂O cannot be obtained quite free from Hg and HgO, this is confirmed by Bruns a O Pfordten (B 21, 2010), who assert that Hg₂O oxidises to HgO at the ordinary temperature Barfoed (J pr [2] 38, 441) says that the product of the action of NaOHAq on mercurous salts is a mixture of Hg, Hg, O, and HgO in varying proportions The descriptions of Hg2O probably apply to Hg.O mixed with more or less Hg and some HgO

Mercurous oxide is a black powder, S G 10 69 (Herapath, P M 64, 321), 8 95 (Karsten, S 65, 894) H.F [Hg²,O] = 24,860 (Thomsen, Z P C 2, 21) Hg₂O is decomposed very easily by light or heat, giving HgO and Hg, strongly heated gives Hg and O Dilute HClAq produces Hg₂O is soluble in cone acetic acid With dilute acids Hg,O generally yields mercurous salts, with H,PO,Aq it gives H,PO,Aq and Hg Bolled with KIAq, Hg and HgI, 2KIAq are formed (Berthemot, J Ph 14, 189) cone. NH ClAq, NH, is evolved and Hg and HgCl, are produced (Pagenstecher, R. P. 27, 27,

Thompson, P. M [8] 10, 179)

Mercuric oxide HgO. (Red oxide of mercury Red precipitate) Mol w unknown, as compound has not been gasified S G 11 074 at 17 5° (Herapath, P M 64, 321), 11 186 to 11 344 at 4° (Playfair a Joule, C S Mem 3, 84, and C J 1, 137), 11 29 at 4° in vacuo (Le Royer a Dumas, in Bottger's Tabellarische Uebersicht der Spec Gewichte der Körper, Frankturt, 1837) S H 19°-52° = 053 (Kopp, T 155, 71), 5°-98° = 0518 (Regnault, A Ch [3] 1, 129) HF [Hg,O] = 22,000 (Thomsen, Z P C 2, 21) Crystallises in rhombic forms a b c = 6523 1 9456 (Nordenskjold, P 114, 621), in monoclini forms, according to Des Cloiseaux (A Ch [4] 20, 201) CE (0°-100°) 0058 (Playfair a Joule, O J 1, 187)

HgO was known to the Arabians in the eighth century, Geber prepared it by calcining the nitrate, and towards the end of the seventeenth century Boyle obtained it by strongly heating Hg in air

Formation —By heating Hg to near its B P in a loosely covered vessel for a long time

Preparation -1 Hg is dissolved in HNO, Aq, the solution is evaporated to dryness, the residue is powdered and then heated on a sand tray so long as N oxides are evolved, the temperature being slowly raised, and the heating continued till a porcelain plate held over the vessel shows a slight deposit of Hg HgO thus prepared a slight deposit of Hg HgO thus prepared forms red lustrous scales —2 One of the oxy chlorides 2HgO HgCl2, and the oxychloride 4HgO HgCl2, when treated with KOHAq, give red HgO, another oxychloride 2HgO HgCl2, and also the oxychloride 3HgO HgCl,, give yellow HgO by treatment with KOHAq The compound 2HgO HgCl, which yields rcd HgO is prepared by mixing 1 vol KHCO₃Aq, free from K₂CO₃, saturated at 15°, with 3 vols HgCl,Aq, also saturated at 15°, stirring with a glass rod till black streaks appear where the rod rubs the glass, pouring off, adding a fresh quantity of the The com mixed solution, and again stirring pound 2HgO HgCl₂ which gives the yellow HgO is prepared by stirring a mixture of 1 vol KHCO₂Aq, saturated at 15°, with 6 to 10 vols HgCl₂Aq, also saturated at 15° The compound 4HgO HgCl₂ is prepared by mixing 1 vol HgCl2Aq (saturated at 15°) with a large excess (4 to 6 vols) KHCO, Aq (saturated at 15°), and allowing to stand for some time (cf Mercury, oxychlorides of, p. 223)—3 Hg(NO,), Aq, or HgCl₂Aq, is poured into KOHAq, the pp is thoroughly washed and dried at 100°-120° HgO thus prepared forms a yellow compact solid

Properties.—HgO exhibits allotropy, it forms heavy, red, crystalline scales, or a somewhat more bulky, amorphous, yellow powder (v supra) HgO is a violent irritant poison HgO is very slightly soluble in water, 1 pt dissolves in 200,000 cold water, or in 125,000 pts if the water is boiled with HgO and then allowed to cool (Wallace, Chem Gazette, 1858, 345) The solution has a metallic taste Heated to redness, Hg is separated into Hg and O Heated below the temperature of decomposition, HgO turns black, but recovers its original colour on cooling. HgO is slowly blackened and decomposed to Hg and O by the action of light There are differences in the reactions of Ol, HgOl, in

| alcoholic solution, and oxalic acid, with the two
varieties of HgO (v. Reactions, Nos. 8, 9, 10)
Reactions — 1 Decomposed by heating to

redness, giving Hg and O, Pelouze (C R 16, 50) said that yellow HgO is decomposed at a lower temperature than the red variety, but this was not confirmed by Gay Lussac (C R 16,309), nor by Millon (B J 27, 112) Carnelley a Walker (C J 53, 80) found that HgO, ppd by NaOHAq from HgCl2Aq, began to give off O at a little above 175°, and that evolution of O became rapid at c 415°, at which temperature red HgO was formed and decomposed. Myers's results (obtained by measuring vapour pressures of O from HgO, B 6, 11) agree with those of C a Debray (C R 77, 123) found that when a tube containing HgO was sealed, and the whole tube was heated to 440°, the O evolved was almost wholly again absorbed -2 A mixture of HgO with such easily oxidised bodies as P, S, Sb, detonates when heated more or less violently Some organic compounds are oxidised by boiling in solution with HgO SO2Aq boiled with HgO produces SO,Aq and Hg SnCl,Aq forms SnCl,Aq and Hg — 3 HgO is decomposed, rapidly and somewhat violently, by heating with magnesium, in the ratio HgO Mg, with formation of MgO and Hg (Winkler, B 23, 128) —4 Heated with sodium, Na amalgam and the compound Na₂O HgO are formed (Beketoff, B 13, 2392), the compound Na₂O HgO is not decomposed by heat, but very quickly by water -5 HgO dis solves in molten potash If the KOH is nearly saturated with HgO, allowed to cool slowly, and lixiviated with a little cold water, a heavy violet crystalline powder and a lighter greyish green powder are obtained The violet powder is said to consist of KO HgO, and the greyish powder to contain from 2 to 5 pc K,O, the SG of K₂O HgO is 1031, it is decomposed at high temperatures, also by continued washing with water, but less completely by alcohol (St Meunier, C R 60, 557) —6 According to Fouberg (A Ch [4] 1, 300), saturated solutions of the alkali and alkaline earth haloid compounds are decom posed, with separation of alkali or alkaline oxides, by boiling with HgO (cf Melsens, A Ch [3] 26, 220, and H Rose, P 107, 298) André, however, says that boiling saturated solutions of alkaline earth chlorides react with HgO to form either oxychlorides xHgCl, yHgO, or compounds of HgO with the alkaline chloride (C R 104, 431, v Mercury oxychlorades of, p 223, and also unfra, Combinations, No 1) According to Jehn (Ar Ph [3] 1, 97), HgO boiled with KIAq produces KOHAq and the double iodide HgI2KI -7 HgO reacts with most acids to form mercuric salts HgX_2 (X = NO_3 , $\frac{1}{2}SO_4$, $\frac{1}{3}PO_4$, &c) -8 The reaction of chlorine with HgO differs according to the conditions, and the variety of HgO used Cl scarcely reacts with red crystalline HgO, with yellow HgO, prepared by ppn and dried at c 100°, Cl reacts energetically forming HgCl₂ and O, with the yellow oxide, dried at 300° and cooled, Ol reacts more slowly, forming Cl₂O and HgCl₂, or, if water be present, forming HClOAq and HgO HgCl₂ (of vol 11 pp 12,16) -9 An alcoholic solution of mercuric chloride heated with yellow HgO at once produces black oxychloride HgO HgOl2, the same oxychloride is formed from the red variety of HgO only after prolonged action of boiling alcoholic HgCl₂ solution—10 Oxalic acid solution reacts with yellow HgO, to form oxalate, in the cold, but the red variety is unchanged when

boiled with H2C2O4Aq

Combinations — 1 With alkaline earth chlorides, obtained by the reaction of HgO with solutions of CaCl₂, BaCl₂, and SrCl₂ The compounds 2HgO CaCl₂4H₂O, HgO BaCl₂6H₂O, and HgO SrCl₂6H₂O, are described by André (C R 104, 431) — 2 With ammonia, to form 2HgO NH₂ H₂O = NHg₂OH 2H₂O, this compound reacts with soids as a base forming dimercuri ammonium salts (v Mercuram Montum compounds, p 206)

Mercury, oxybromide of 8HgO HgBr₂
= Hg₄O₃Br₂ (Basic mercuric bromide) A
yellow, crystalline, powder, obtained by boiling
HgBr₄A with HgO, filtering, and allowing to
crystallise, or by partial ppn of HgBr₂Aq by
KOHAq, and boiling the liquid in contact with
the pp (Lowig, P 14, 485, cf Rammelsberg,
P 55, 248)

For H F of oxybromides of Hg v André, Bl

[2] 41, 274

Mercury, oxychlorides of Hg.O_yCl. (Basic mercury chlorides) Several oxychlorides of Hg are known, they are produced by the reaction of HgO with HgCl,Aq, by partial ppn of HgCl,Aq by KOHAq or NaOHAq, by mixing KHCO₃Aq and HgCl,Aq in different proportions, and by the reaction of Cl with yellow HgO

and by the reaction of Cl with yellow HgO

Millon (A Ch [3] 27, 253) described oxychlorides obtained by mixing solutions of KHCO, (free from K,CO,) and HgCl, both saturated at 15° (1) 2HgO HgCl, by adding 1 vol KHCO,Aq to 6-10 vols HgCl,Aq, also by adding 1 vol KHCO,Aq to 3 vols HgCl,Aq, stirring till ppn begins on the sides of the vessel, pouring off the liquid, adding a fresh quantity of the same mixture, and stirring again The compound obtained by the first process forms a red non crystalline powder, and yields yellow HgO when acted on by KOHAq, as obtained by the second process, the compound is a heavy, black, lustrous solid, which yields red HgO with KOHAq (ii) 3HgO HgCl, by mixing equal volumes of the solutions of KHCO, and HgCl, and allowing to stand, a golden yellow crystalline pp, yielding yellow HgO with KOHAq (iii) 4HgO HgCl, by mixing 1 vol HgCl,Aq with 4-6 vols KHCO,Aq, and allowing to stand, a brown crystalline solid, which yields red HgO with KOHAq

Roucher (A Ch [3] 18, 372) described seven oxychlorides, containing HgCl₂ and HgO in the ratios 1, \frac{1}{2}, 2, 3, 4, 5, and 6, each oxychloride exists, according to Roucher, in two varieties, one derived from and giving red HgO, the other derived from and giving yellow HgO, some of the oxychlorides also exhibit other differences Roucher described 15 different oxychlorides. A tabular statement showing the other differences between the oxychlorides is given by Roucher

André (O R 104, 431) described two oxychlorides, HgCl, 8HgO and 2HgCl, 8HgO, obtained by dissolving HgO in boiling CaCl,Aq and MgCl,Aq, respectively, and pouring the solutions into large quantities of cold water.

The oxychlorides of Hg have been examined more recently by Thümmell (Ar. Ph. 27, 589, v.

abstract in C J 56, 1050) f. says that only 5 definite compounds exist, viz, HgO 2HgCl₂, HgO HgCl₂, 2HgO HgCl₂, 3HgO HgCl₂, and HgO HgCl., 2HgO HgCl., 3HgO.HgCl., and 4HgO HgCl., (1) HgO 2HgCl. is formed in all solutions prepared by dissolving HgO in HgCl.Aq, but it is readily decomposed, it is HgO HgCl₂, 4HgO HgCl₂ best prepared by heating at 100° 1 pt HgO (red or yellow), with 10 pts HgCl₂, and 60 pts water, stirring till no further separation of a yellow powder occurs, washing, drying, and then washing with ether (free from alcohol) to remove HgCl₂ Walm water separates 2HgO HgCl₂, NaOHAq ppts rcd HgO (11) HgO HgCl₂ has NaOHAq ppts rcd HgO not yet been obtained pure (iii) 2HgO HgCl₂ exists in two varieties, (a) red variety, obtained by mixing solutions of NuHCO, and HgCl₂ in the ratio 2NaHCO, HgCl, (b) black variety, obtained by heating the red variety when dry, or by adding HgO to hot HgCl, Aq, or by mixing equivalent quantities of red HgO and HgCl, in cold water, or by treating 3HgO HgCl, with cold HgCl₂Aq (iv) 3HgO HgCl₂ is a yellow pp obtained by adding alkaline carbonate (normal or acid) to HgCl,Aq, avoiding excess of the carbonate, also by treating freshly ppd yellow HgO with HgCl Aq (this preparation is yellow and yields yellow HoO with KOHAq), also by treating washed red HgO with HgCl Aq (this preparation is reddish yellow and yields red HgO by KOHAq) (v) 4HgO HgCl, is obtained as a brown amorphous powder, by adding KHCO₃Aq to HgCl₂Aq, in the ratio 30 to 35 KHCO, HgCl, it is also obtained, as reddishbrown crystalline plates, by shaking HgCl Aq with red HgO in the ratio HgCl, 6HgO, both varieties give yellow HgO by KOHAq All these oxychlorides yield sublimates containing HgCl and HgCl when heated

For H F of oxychlorides of Hg v André, Bl

[2] 41, 274

Mercury, oxycyanides of, v. Cyanides, vol.

n p 342

Mercury, oxyfluoride of HgO HgF₂H₂O. (Basic mercuric fluoride) A yellow crystalline solid, obtained by dissolving freshly ppd HgO in HFAq, and digesting the solution with HgO, or evaporating the solution (Finkener, P 110, 628) The oxyfluoride is also obtained by heating HgF₂2H₂O (q v p 210) to 30° (F) Heated above 100°, the oxyfluoride gives off HO and HF, it is decomposed by water with separation of HgO

Mercury, oxynodide of 3HgO HgL. (Basic mercuric vodule) A yellowish brown solid, obtained by melting together HgO and HgL. in the ratio 3HgO HgL., also by digesting HgL, with dilute KOHAq (Rammelsberg, P 48, 182)

Mercury, oxysulphides of Oxysulphides of Hg have been described, but according to Polleck (B 22, 2859) none has been isolated, and the existence of any is very improbable Mercury, phosphide of No phosphide of

Mercury, phosphide of No phosphide of Hg has been isolated with certainty By passing P hydride, prepared by boiling amorphous P with KOHAq, into HgCl₂Aq, several compounds have been obtained Aschan (Chem Zeitung, 10, 82, 102) describes a yellow compound 3Hg₂P₂,7HgCl₂, a red compound 4Hg₃P₂,5HgCl₂, and a black compound Hg₂P₂HgCl₂. A compound probably 2PH, 6Hg₂O is said by Aschan (Le) to be formed by passing P hydride over Hg₂CO₂. The pra-

when P hydride is passed into Hg(NO₂),Aq are probably mixtures of different compounds of Hg, P, and HNO_s (A) Most of the foregoing compounds are readily decomposed,

some explosively, by warming

Mercury, salts of Hg forms two series of salts, mercurous salts corresponding with Hg2O, and mercuric salts corresponding with HgO The former are obtained sometimes by dissolving Hg₂O in acids, sometimes by dissolving Hg in acids and digesting with excess of Hg, and in some cases by double decomposition from the nitrate, the mercuric salts are obtained by dia solving HgO or HgCO, in acids, or by double decomposition from the nitrate. The mercurous salts have the composition HgX, where X = NO₃, 2SO, &c , the mercuric salts have the composition HgX2 The mercuric salts are more stable, as a class, than the mercurous salts mal mercurous salts are generally decomposed by water into a basic salt, which separates, and an acid salt, which goes into solution Many basic salts and a large number of double salts are known The salts of Hg, as a class, act as violent and irritating poisons The principal salts of Hg are the following (v Carbonates, Ni The principal TRATES, SULPHATES, &c) antimonates, arsenates and -ites, bromates, carbonates, chlorates and perchlorates, chromates, rodates and periodates, molybdates, nitrates and ites, phosphates, selen ates and -ites, sulphates and -ites, tantalates,

throsulphates, tungstates, vanadates
Mercury, selenide of HgSe Small quan tities of more or less pure HgSe occur native in the Harz, accompanying PbSe HgSe 18 produced by strongly heating together Hg and Se, and subliming at a higher temperature, forms grey, metal like, lustrous laminæ, dis solved by aqua regia with formation of Hg selenite, slowly changed to the same compound by boiling cone nitric acid (Uelsmann, A 116, 126, cf Little, A 112, 211) HgSe is also formed by passing H2Se for a long time into HgCl2Aq, the white pp of 2HgSe HgCl, at first produced is changed to black HgSe S G of natural HgSe 18 7 1 to 74, SG of artificially prepared HgSe

IS 8 877

Combinations -1 With mercuric chloride, to form 2HgSe HgCl₂, a white pp formed by adding H₂Se, or K₂Se, to excess of HgCl₂Aq -2 With mercuric oxide, to form 2HgSe HgO, a black powder formed by treating 2HgSe HgCl₂ with NaOHAq Decomposed by heat, yielding sublimates of HgSe and Hg (Uelsmann, A 116,

Mercury, selenochloride of Hg, Se, Cl, v Mercury, selenide of, Combinations, No 1

Mercury, selenosulphide of A mineral approaching the composition HgSe 4HgS is found near San Onofre in Mexico, it is known as onofrite

Mercury, selenocyanides of. HgSeCy and Hg(SeCy)2, v vol n p 348

Mercury, silicofluorides of Two are known, Hg₂S₁F₄ 2H₂O and HgS₁F₆ 6H₂O

MERCUBOUS SILICOFLUORIDE, Hg2S1F4 2H2O Olear prismatic crystals, obtained by dissolving Hg.CO. in H.SiF.Aq, evaporating, washing with a little water, and pressing between paper (Finkener, P. 111, 246, of Berzelius, P. 1, 200).

MERCURIC SILICOFLUORIDE, ? HgS:F, 6H,O. Obtained by dissolving HgO in H₂SiF₆Aq, eva porating till yellow needles (HgSiF₆ HgO 3H₂O) begin to separate, and then allowing to stand at a temperature not above 15° Forms clear, colourless, rhombohedral crystals, very un stable, deliquescent in air, and efflorescent over H,SO,, composition doubtful (Finkener, P 111, 246) The compound HgSiF, HgO 3H,O (Finkener) was described by Berzelius (P 1, 200) as the normal salt

Mercury, sulphides of Two are known, Hg2S and HgS, the latter reacts towards the alkalı sulphides as an acidic sulphide, it also combines with many Hg compounds to form

double compounds

MERCUROUS SULPHIDE, Hg,S This sulphide is best prepared, according to Berzelius, by dropping mercurous acetate solution into Na or NH, sulphide solution (cf Brande, Q J S 18, 292) HgNO₈Aq should not be used, as the HNO₃ produced oxidises the Hg₂S Hg₂S is a black powder, easily decomposed by heat to HgS and Hg According to Barfoed (Bl [2] 3, 183) the substance described as Hg₂S always contains some Hg, however it may be prepared

MERCURIC SULPHIDE, HgS Mol w uncertain H F [Hg,S] = 8,220 (Thomsen, Z P C 2, 21) This compound exists in two forms a black amorphous pp, and a red crystalline body

known as vermilion or cinnabar

Occurrence - In Illyria, Spain, Bohemia, Ural mountains, China, Japan, Mexico, California, Chili, and Peru

Formation —1 By rubbing or heating to gether 1 pt S and 61 pts Hg -2 By adding H₂S, or an alkaline sulphide, to solution of a mercuric salt -3 By digesting Hg with an al kaline polysulphide -4 By subliming a mixture

of S and HgO or HgSO.

Preparation -1 Amorphous black mer curic sulphide is prepared by passing excess of H,8 into slightly acidined HgCl,Aq or Hg(NO_s),Aq, washing the pp thoroughly with dilute HNO_sAq and then with water, and drying at a low temperature -2 Red crystalline mercuric sulphide (vermilion) is prepared in different ways (a) A mixture of 6 pts Hg and 1 pt S is heated till combination occurs (attended generally with production of heat and light and partial projection of the mass), the product is powdered, mixed with a small quantity of S, and heated for some hours in a hard glass flask, sunk in sand in a wind-furnace, the flask is loosely closed by a charcoal stopper and is arranged so that the upper part is kept com paratively cold, red HgS sublimes on to the neck of the flask The HgS is purified by grind ing, boiling with KOHAq, and washing with water (b) Black amorphous HgS is heated with an alkaline persulphide This may be done by triturating 100 pts Hg with 38 pts 8 for some hours, till black HgS is produced, heating with 25 pts KOH in 130-150 pts water to 45°-50° for several hours (the water being replaced as it evaporates, and the mass being stirred from time to time) until reddening begins, after which the temperature is maintained at 45° till the whole is bright red The red HgS is washed, and any Hg present is removed by levigation (Brunner, P. 15, 598, of. Doberemer, S 61, 380; Firmenich, D P J 172, 370, Liebig, A 5, 289, 7, 49, Raab, N R P 24, 39) (c) HgCl₂Aq is poured into excess of dilute NH₂Aq, to the pp of NH₂HgCl thus produced is added conc Na₂S₂O₂Aq in quantity rather more than sufficient to dissolve the pp, and the whole is heated for some time to 70°-80° (Hausmann, B 7, 1746) For details of the manufacture of Vermilion v Dictionary of Applied Hermistry—8 Colloidal mercuric "ulphide, soluble in water, is obtained by ppg a dilute solution of a mercuric salt by H₂S, and washing with water of dilute H₂SAq for a long time (Winssinger, Bl [2] 49, 452)

Properties -The black sulphide is an amorphous, heavy powder, heated in a closed vessel, it yields a sublimate of red HgS, heated in air, Hg sublimes and SO₂ is formed, it is not acted on by dilute acids. The red sulphide crystallises in hexagonal forms, $a c = 1 \ 1 \ 145$, SG 81 to 899, polarises light, blackens by exposure to light (v Heumann, B 7, 750), heated to the sublimation temperature, red HgS is changed to the black variety (Fuchs, P 31, 581) Mitscherlich (A 12, 168) found V D of HgS at 670° to be 85 3, V and C Meyer found VD at 1560° to be 78, the formula HgS requires V D 116, a mixture of Hg+Hg+2S requires V D 773 The red sulphide reacts with acids The colmore slowly than the black variety loidal sulphide is soluble in water, forming a solution which is black and opaque when cone, but brown, with a greenish tint by reflected light, when dilute, a very dilute solution may be boiled till all H2S is expelled, or kept for some time, without change

Reactions -1 Heated in a closed vessel, HgS sublimes -2 Heated in air, SO2 is formed, and Hg sublimes -3 Heated with solid alkahs or alkaline carbonates, Hg sublimes and alkaline sulphide remains—4 Heated with eron, tin, antimony, copper, sinc (and some other metals), a metallic sulphide and Hg are produced, HgS is decomposed by heating with finely divided Cu and water (v Heumann, B 7, 1388, 1486) -5 Digested for some time with sodine in KIAq, HgS is decomposed with formation of HgI, 2KI and separation of S (Wagner, J pr 98, 23) -6 HgS is decomposed to Hg and SO, by heating with lead monoxide, Pb being separated .- 7 HgS is scarcely attacked by dilute acids, conc nitric acid produces Hg(NO₃) mixed with HgSO₄, HNO, Aq S G o 12 produces a white compound 2HgS Hg(NO,)2 -- 8 According to Bolley (A 75, 239) HgS is at once decomposed by an ammoniacal solution of silver nitrate, with forms tion of a mercurammonium salt and Ag.S -9 HgS is insoluble in caustic soda or sodium monosulphide solution, but it dissolves in a mixture of the two, ie in sodium hydrosulphide solution This solution contains a sulpho-salt (sulpho-hydrargyrate of sodium) The solution is readily obtained by adding KOHAq to ppd HgS, and passing in H₂S (excess of H₂S causes reppn of HgS) On evaporation, white crystals HgS K₂S 5H₂O separate, mixed with KOH, these crystals are decomposed by water (Weber, P 97, 76, of Brunner, P 15, 596) By ppg HgCl_Aq with NH, sulphide, and adding KOHAq, a solution is obtained, which, on evaporation, yields KCl, and then a sulpho- salt mixed with KOH. Vol. III.

According to Schneider (P 127, 488) the crystals of the sulpho-salt, when kept for some years in KOHAq, form six sided, lustrous, olive green tablets having the composition 2Hg8 K₂S

Combinations—1 With alkah sulphides, v

supra, Reactions No 9—2 Forms a compound with hydrogen sulphide, 31HgS H₂S Produced in solution by passing H₂S into HgS suspended in boiled water (Linder a Picton, C J Proc 1890 49) -3 With cuprous chloride to form 2HgS Cu2Cl2, a yellow solid, obtained by boiling HgS with CuCl.Aq and HClAq, and removing S by $_{1}$ CS. $_{2}$ (?3HgS + $_{2}$ CuCl. $_{2}$ = 2HgS Cu. $_{2}$ Cl. $_{2}$ + HgCl. $_{2}$ + S) This compound is decomposed by boiling cone HClAq with evolution of a little H₂S and forms tion of Cu₂Cl₂ and HgCl₂ in solution, dilute hot H2SO4Aq has no action, but with boiling cone H₂SO₄, HCl and SO₂ are evolved and a compound of HgSO, and HgS is formed NaOHAq produces NaCl, HgS, and Cu_2O (v Heumann, B 7, 1390) 4 With mercuric chloride, and also with mercuric bromide, to form compounds 2HgS.HgX₂ (X = Cl or Br) These sulphohaloid compounds are formed (a) by passing H2S into excess of HgCl₂Aq or HgBr Aq, (b) by digesting freshly ppd HgS with boiling HgCl₂Aq or HgBr₂Aq (H Rose, P 13, 59), (c) by adding HCl (or HBr), or solution of a metallic chloride (or bromide), to HgS dissolved in mercuric acetate solution (Palm, C C 1863 120), (d) by heating HgS with 8-10 parts HgCl₂ or HgBr₂, till the whole melts, and washing the cold mass with boiling water (Schneider, P 115, 167) The compounds are yellow white crystalline powders, decomposed by slow heating to HgS and HgX, decomposed by alkalı solutions, but not by HNO.Aq or H.SO.Aq (of Barfoed, J pr 93, 230) -5 With mercuric sodule to form the sulpho nodide HgS HgI,, a yellow solid ob tained by digesting HgI, with less H,SAq than suffices for complete decomposition (H. Rose, P. 13, 59), also by ppg HgO and Hgl, in HClAq by a small quantity of H₂S (Rammelsberg, P 48, 175), also by saturating HgI₂ in HIAq with H₂S, and diluting (Kekulé) Palm (C C 1863 121) says that the yellow red pp obtained by adding HIAq, or a solution of an alkalı iodide, to HgS dissolved in mercuric acetate solution, has the composition 2HgS HgI,-6 With mercuric fluoride, to form the sulphofluoride 2HgS HgF₂, obtained by passing a little H₂S into HgF₂ dissolved in HFAq (H Rose, P 13, 59) —7 With mercure sulphate, to form several the chief of which are compounds, (2) HgSO, 2HgS, and (3) These compounds are obtained, HgSO, HgS, HgSO, 3HgS (1) by treating red HgS with warm H2SO.Aq Palm, J 1862 220), (2) by treating 2HgS HgNO. (obtained by passing a little H₂S into Hg(NO₃)₄Aq) with H₂SO₄Aq (Barfoed, J 1864 282, Kessler, A Ch [2] 6, 61ō), (3) by adding H₂S₄O₈Aq to Hg(NO₂)₂Aq and removing S by washing with CS₂ (Spring, A 199, 116, Wacken roder, A 60, 190) -8 With mercuric nutrate, to form 2HgS Hg(NO₃)₂, a white solid, obtained by passing a little H₂S into Hg(NO₃)₂Aq, or by digesting freshly ppd HgS with Hg(NO₃)₂Aq. by HNO.Aq or alkalı nitrate solution (H Rose, Barfoed, Palm, Le)

By heating HgS with HNO.Aq, S.G. 1 2, to 120° in a closed tube, Gramp (J pr [2] 14, 299) obtained a white crystalline mass of 6HgS HgO 2Hg(NO_s)₂ 1.2H₂O

Mercury, sulphobiomide of, v Mercuric sulphide, Combinations, No 4

Mercury, sulphochloride of, v Mercuric sulphide, Combinations, No 4

Mercury, sulphocyanides of, v vol ii p

Mercury, sulphofluoride of, v. Mercuric sulphide, Combinations, No 6

Mercury, sulpho-10dides of, v Mercuric sulphide, Combinations, No 5

Mercury, sulphoselenide of, v Mercury, selenosulphide of, p 224

MMP MERCURY COMPOUNDS, ORGANIC Mercury forms compounds with two identical alcohol radicles, or with one alcohol radicle and one acid residue Compounds of mercury with two different alcohol radicles appear to split up at the moment of their formation, eg 2HgEtMe = HgMe₂ + HgEt₂ (Frankland, A 111, 57)

Mercury dimethide Hg(CH₃), Mercury dimethyl Mol w 230 V D 8 29 (cale 7 97) (93°-96°)

Formation —1 When mercury is exposed with MeI to sunlight for a week, crystalline CH₂HgI is formed (Frankland, A 85, 361) When this body is distilled with KOH, hime, or KOy, mercury dimethide passes over as a heavy liquid which may be purified by washing with water and rectifying over CaCl₂ (Buckton, Pr 9, 91, A 108, 103) —2 By the action of sodium-amalgam on MeI (10 pts) in presence of acetic ether (1 pt) (Frankland a Duppa, C J 17,415,

A 130, 105)

Properties — Colourless oil, with faint but mawkish taste Insol water, v sol alcohol and ether Dissolves phosphorus, resins, and caout chouc Very inflammable, burning with a bright flame

Reactions - 1 Iodine forms CH₃HgI and methane Bromine acts in like manner -2 SnCl, forms a crystalline compound which is decomposed by water with formation of CH₂HgCl -8 Conc HClAq gives methane and CH₂HgCl -4 Conc H₂SO₄ gives methane and (CH₂Hg)₂SO₄ -5 PCl₃ gives CH₂HgCl -6. KMnO₄ oxidises it to CH₂Hg OH (Seidel)

Mercuric chloro-methide CH, HgCl [1709] (Seidel, J pr [2] 29, 135) S G 4 063 (Schröder, B 12, 563) Formed from HgMe, by the action of HCl Lamins

Mercuric codomethide CH, HgI [143°] From MeI and Hg in sunlight (Frankland) Formed also by heating HgMe2 with HgI2 Small nacreous lamins (from ether), insol water, m sol alcohol, v sol ether and MeI Slightly volatile, emitting an unpleasant odour, and leaving a persistent nauseous taste May be sublimed.

Mercuric nitromethide CH₂ HgNO₂ [1007] From an alcoholic solution of CH₂ HgI and AgNO₂ Nacreous lamine, v sol water, sl sol alcohol Its solution is not ppd by KOH or baryts water, but HCl and soluble chlorides ppt CH₂HgCl (Strecker, A 92, 79)

Mercuric acetomethide CH, Hg.OAc [143°] Obtained by heating HgMe, with acetic acid at 180° (Otto, Z. [2] 6, 25) Thin tables,

with very offensive odour, nearly insol boiling water and cold HOAc

Mercurse chloro-methylo rodide CH₂Cl HgI [129°] Obtained by boiling CH₂I HgI with alcoholic HgCl₂ (Sakurai, C J 41, 360) Silky plates (from alcohol) Decomposed by rodine into methylene chloro rodide and HgCl₂

Mercuric todo methylo-todide CH₂I HgI [109°] Formed by leaving mercury and a little mercurous rodide in contact with methylene rodide in a sealed tube for several days (Wanklyn a Von Than, C J 12, 258, Sakurai, C J 37, 658) White crystals (from CH₂I₂), insol water, cold alcohol, ether, chloro form, EtI, and benzene, sl sol boiling alcohol, v sol methylene rodide When heated with rodine dissolved in aqueous KI it is decomposed into CH₂I₂ and HgI₂ Chlorine and bromine act in like manner When heated with HClAq it is reduced to CH₂ HgI

D1-mercuric methyleno-ds-sodide CH₁(HgI)₂: [c 230°] Obtained by exposing a mixture of an ethereal solution of methylene iodide with a little HgI, and an excess of mercury to sunlight (Sakurai, C J 39, 487) I ormed also by the action of mercury on CH I HgI Yellowish crystalline powder, insol all ordinary solvents, sl sol hot methylene iodide When heated with dilute HClAq or with KIAqit yields CH₂ HgI Iodine forms HgI₂ and methylene iodide

Mercuric methenylo-trs-todide CH(HgI), From iodoform, mercury, and alco hol, by exposure to sunlight (Sakurai, C J 39, 488) Yellow mass, insol ordinary solvents and in CH₂I₂. Gives iodoform when treated with iodine

Mercurie diethide HgEt. Mol w 258 (159°) SG 246 VD 997 (cale 94) Strecker (C R 39, 57, A 92, 97) by acting on I tI with mercury obtained the compound EtHgI Dun haupt (Chem Gaz 1854, 263, A 92, 879) obtained the corresponding EtHgCl and LtHgBr by decomposing bismuth triethide with HgCl, or HgBr. Buckton (A 109, 218, C J 16, 17) obtained HgEt, by the action of ZnEt, on HgCl, and, lastly, Frankland and Duppa showed that mercuric diethide can be more easily obtained by the action of sodium amalgam on EtI in presence of acetic ether. The acetic ether remains in undiminished quantity at the end of the process, but nevertheless its presence is essential

Preparation — Ethyl nodide (10 pts) is mixed with EtOAc (1 pt) and poured upon pc sodium amalgam, the flask being shaken and cooled in water. When separation of NaI has rendered the liquid pasty it is distilled off from a water bath and shaken with fresh amalgam Finally it is mixed with water, and the oil dried over CaCl, and rectified.

Properties - Transparent colourless liquid, with faint ethereal odour, insol water, sl sol, alcohol and ether Very poisonous Burns with smoky flame Takes fire in chlorine.

Reactions.—1 Acts violently on bromine and todine, forming EtHgBr and EtHgI (Buckton, A 112, 220)—2 Alcoholic HgCl₂ forms EtHgCl. 3 Cone HClAq forms ethane and EtHgCl—4 H₂SO₄ gives ethane and (EtH_C)₂SO₄—5. Sedium forms a bulky grey spongy mass, which

takes fire in air and violently decomposes when | heated -6 Heated with finely granulated zinc it yields ZnEt, and mercury (Franklanda Duppa, C J 17, 29) Cadmium forms CdEt, Bismuth gives BiEt, -7 Mercuric ethide is decomposed when heated at 150° with copper, iron, silver, or gold, but ethides of these metals are not formed 8 KMnO, forms EtHgOH - 9 When heated with PCl_s it forms PEtČl₂—10 Iodoform at 90° gives acetylene and ethylene (Suida, M 1, 716)

Mercuric chloro-ethide EtHgCl [190°] (Seidel) SG 348 Formed by the action of HgCl2 on BiEt2, by 'reating HgEt2 with alcoholic HgCl₂, and by the action of HgCl₂ on ZnEt₂ Ppd by adding NaCl to an aqueous solution of EtHgNO, with HCl Obtained also by treating EtHgOH Light iridescent laminæ (from al cohol) Nearly insol water, sl sol ether, v sol boiling alcohol Sublimes at 40° With Ag CO. it gives (EtHg)₂CO₃, which crystallises with difficulty and is easily decomposed by heat and by acids Ag₃PO₄ gives a very soluble phosphate (Dunhaupt)

Mercuric iodomethide EtHgI Formed by the action of mercury on EtI in diffused daylight Decomposed by direct sunlight (Strecker, A 92, 75) Shining laminæ, insol water, sol alcohol and ether Sublimes at 100° Dissolves without change in aqueous NH₃ or KOH

ZnEt, it yields ZnI, and HgLt,

Mercuric ethylo hydroxide EtHgOH Obtained by adding moist Ag O to a boiling al coholic solution of EtHgCl, filtering, and evapo rating in vacuo Strongly alkaline liquid, which V sol water blisters the skin Decomposes ammonium salts with expulsion of NH3 It does not liberate KOH or MgO from their salts, but it ppts salts of Al, Zn, Sn, Cu, Au, and Pt a large excess of H2S it forms a white pp turning through orange to black With metallic zinc it forms ZnEt, With acids it forms crystalline salts, eg HCl yields EtHgCl

Mercuric bromo ethide EtHgBr Mercuric ethylo bromide Formed from BiEt, and HgBr2, or by treating EtHgOH with HBr (Dun-

haupt, A 92, 379) Resembles EtHgCl

Mercuric ethylo cyanide EtHgCy Formed by saturating an alcoholic solution of EtHgOH with HCy Crystallises readily, v sol alcohol and ether Very volatile Gives off a repulsive odour when heated

Mercuric ethylo nitrate EtHgNO, Mercuric nitro ethide From EtHgI and AgNO. Colourless prisms, v e sol water, m sol alcohol

(Strecker)

Mercuric ethylo sulphate (EtHg), SO. Formed from EtHgCl and Ag2SO, Shining

laminæ (from alcohol)

Mercuric ethylo sulphide (EtHg)28 Obtained by adding ammonium sulphide to an alcoholic solution of EtHgCl Yellowish white powder, v sol alcohol, ether, and CS₂ The al coholic solution is decomposed by evaporation, leaving HgS

EtHgOAc Mercurio ethylu-acetate Obtained by dissolving HgEt, in HOAc [178°]

(Otto, Z 1870, 25)

Mercuric dipropyl HgPr, (190°) (0); (180°) (Schtscherbakoff, J R 13, 353) S G 12 2 214 Formed by the action of propyl iodide on sodiumamalgam in presence of acetic ether (Cahours,

C. R 76, 133, 1383) Oil, sl sol alcohol, v sol. With iodine and bromine it forms proether ducts which may be crystallised from alcohol The effect of small additions of HgPr2, of $Hg(C_4H_9)_2$, of $Hg(C_5H_{11})_2$, and of $HgPh_2$ on the freezing point of ethylene bromide has been

studied by Louise and Roux (C R 107, 600) Mercuric di isobutyl Hg(CH₂Pr)₂. (206°) Obtained by treating a mixture SG 1-1835 of isobutyl iodide and acetic ether with 2 pc sodium amalgam (Cahours) Colourless liquid Iodine forms CH, Pr HgI, whence Ag, O forms CH. Pr HgOH Bromine acts in like manner

Mercuric di isoamyl $Hg(C_5H_{11})_2$ SG \circ 1 666 From isoamyl iodide (5 pts), acetic ether (1 pt), and sodium amalgam (Frankland a Duppa, A 130, 110) Colourless oil, decomposed on distillation even in vacuo May be distilled with steam Insol water, v sl sol alcohol, v sol ether With chlorine it forms dense fumes of $C_aH_{11}HgCl$ It reacts with great violence with bromine and iodine With an alcoholic solution of HgCl₂ it readily forms C₃H₁₁HgCl [86°], which crystallises from alcohol in hair like needles An ethereal solution of $Hg(C_5H_{11})_2$ treated first with an alcoholic solution of iodine and then with solid iodine forms isoamyl iodide and C,H,,HgI [122°], which crystallises from alcohol in pearly scales With zine at 130° C₃H₁₁HgI forms zine isoamyl and zinc amalgam

Mercuric di octyl $H_g(C_gH_{17})_2$ S G 17 1 342 Prepared by the action of sodium amalgam on octyl iodide in presence of a little acetic ether (Eighler, B 12, 1880) Liquid Insol water, sol alcohol, ether, and C_bH_b Decomposes at 200° into Hg and hexadecane (dioctyl)

Mercuric octylo rodide C,H,HgI white Prepared by the action of an alco holic solution of iodine on mercury dioctyl

Mercuric octylo chloride C_sH₁₇HgCl White pp Prepared by the action of mercuric

chloride on mercury dioctyl

Mercuric octylo-hydroxide C.H.,HgOH [75°] Prepared by the action of silver oxide on an alcoholic solution of mercury dioctyl (Eichler, B 12, 1881) Yellow leaflets Insol cold, sl sol hot, water, v sol alcohol Alkalıne

Mercurio allylo-todide C,H,HgI [135°] 8 (CS₂) 187 at 49° Formed by shaking allyl nodide with mercury, and extracting the resulting vellow mass with hot alcohol or ether (Zinin, A It is best 96, 363, cf Linnemann, A 140, 180) to mix the allyl iodide with an equal volume of alcohol (Oppenheim, B 4 670) Silvery scales, which turn yellow on exposure to light, especially on arying It even turns yellow in the dark Sublimes at 100° Sl sol cold alcohol, nearly insol water Decomposes above its melting point AgNO₃ added to its alcoholic solution ppts all the iodine as AgI Moist Ag₂O ppts AgI, and the filtrate on evaporation leaves a strongly alkaline syrupy mass which forms salts with acids HI easily decomposes it, forming HgI, and propylene Icdine forms HgI, and allyl iodide (Linnemann, A 133, 133, Suppl 3, 262) PBr, acetyl chloride, and BzCl have no action on mercury allyl iodide On shaking it with a solution of ZnEt, in ether an energetic reaction sets in, the products being mercury, ZnI2, diallyl, and HgEt2. A solution

of KCy acts quickly in the cold, forming diallyl, mercury, HgCy2, and KI, if in distilling off the diallyl the distillation is not stopped in time an explosion occurs Aqueous KI at 100° forms mercury, diallyl, and KHgI_s The mercury allyl compounds attack the skin, producing blisters which appear after the lapse of 7 hours The compound C₃H₅HgCl obtained by the action of HCl on the hydroxide is sparingly soluble (Krasowsky, Z 6, 527)

Mercuric propargyl iodide CaHaHgI From propargyl 10dide and mercury (Henry, B 17, 1132) Small yellowish crystalline masses

diphenyl $Hg(C_6H_5)_2$ Mercuric SG 2318 Formed by heating a (above 300°) mixture of bromo benzene, benzene, HgCl₂, and sodium (Michaelis a Reese, B 15, 2876) Presodium (Michaelis a Reese, B 15, 2876) Prepared by boiling for some time a solution of bromo-benzene (10 pts) in an equal volume of xylene with 2 7 p o sodium amalgam and a little acetic ether (1 pt) The product is recrystallised from benzene (Dreher a Otto, Z [2] 4, 685, 6, Small white needles or prisms, 9, A 154, 93) turning yellow in daylight Insol water, v sol chloroform, CS,, and benzene, m sol ether and boiling alcohol May be sublimed Partly decomposed on distillation into mercury, diphenyl, benzene, and charcoal

Reactions -1 Dry HCl gives benzene and HgCl₂. HI, nitric acid, HBr, and H₂SO₄ act in like manner—2 When melted with sulphur (2 at) the products are HgS and phenyl mercaptan —3 Iodine (2 at) in alcoholic or CS₂ solution forms PhHgI and iodobenzene Excess of nodine forms HgI, and nodo benzene -4 Chlorine forms PhHgCl and chloro benzene. Br acts in like manner -5 Glacial acetic acid yields benzene and PhHgOAc -6 Aluminium forl at 130° forms AlEt, [230°] (Friedel a Crafts, A Ch [6] 14, 460) —7 Alcoholic HgCl₂ at 100° gives PhHgCl -8 When boiled with sodium, benzene and sodium amalgam are formed -9 SO₃ gives mercuric benzene sulphonate (Otto, Jpr [2] 1, 179) -10 Allyl wodide forms diallyl, diphenyl and PhHgI (Suida, *M I 715*) -11 C.H.SO.cl at 160° forms C.H.SO.c.H. and PhHgCl (Otto, *B* 18, 246) -12 COCI CO.Et forms phenylglyoxylic ether (Claisen a Morley, B 11, 1596) 18 When oxidised by KMnO₄ the hydroxide PhHgOH is probably first formed, but on adding HCl this is changed to PhHgCl (Seidel, J pr [2] 29, 134, Otto, J pr [2] 29, 136)

Mercuric phenylo chloride CaH, HgCl Mercuric chlorophenylide [250°] Obtained by slowly passing chlorine over HgPh2 or into its solution in CS, Prepared by heating HgPh, with HgCl, in alcoholic solution at 110° metric tables (from benzene) May be sublimed. SI sol alcohol and benzene, insol water

Mercuric phenylo-bromide C.H.HgBr [275°] Resembles the preceding in preparation and properties Br forms HgBr, and bromobenzene When heated with an alcoholic solution of K.S the products are KBr, HgS, and HgPh.

Mercuric phenylo-rodide C.H.HgL. [266°] From HgPh, and I in alcohol Satiny tables (from alcohol benzene) Insol water, nearly insol. cold alcohol, ether, and benzene, m. sol. hot benzene and chloroform, v. sol. CS.

May be partially sublimed Sodium amalgam reduces it in alcoholic solution to HgPh,

Mercuric phenylo hydroxide C.H.HgOH. From PhHgCl by boiling with alcohol and moist Ag₂O White trimetric prisms (from alcohol), sol boiling water, alcohol, and benzene, sl sol cold water Softens at 160°, but is not melted at 200° The aqueous solution is alkaline in reaction Expels NH, from its salts, ppts alumina from alum, and absorbs CO₂ from the air

Mercuric phenylo cyanide PhHgCy. [204°] From HgPh, and HgCy, in alcoholic solution at 128° Long slender trimetric prisms, v sl sol boiling water, m sol boiling alcohol and benzene Cone HClAq at 120° forms HgCl, formic acid, benzene, and NH₃ Alcoholic KOH forms mercury, benzene, and potassium cyanate Iodine forms PhHgI and ICy H2S forms HgS, benzene, and HCy

Mercuric phenylo-sulphocyanide PhHgSCy [227°] From HgPh and Hg(SCy). Silky plates, sol boiling alcohol

Mercuric phenylo-nitrate PhHgNO. [c 167°] From PhHgCl and AgNO, in alcohol Trimetric silky plates, v sl sol boiling water Conc HClAq gives benzene and mercuric nıtrate

Mercuric phenylo carbonate (PhHg)2CO3 From PhHgCl and Ag2CO3 Small white needles, sl sol boiling water, m sol boiling alcohol and benzene Not decomposed on fusion

Mercuric phenylo-formate
PhHgO CHO [171°] From HgPh, and concentrated formic acid Small tables

Mercuric phenylo acetate PhHgOAc. [149°] Obtained by boiling HgPh, with excess of HOAc, ppg with water, and crystallising from hot water Radiate groups of prisms, sl sol cold, m sol hot, water, m sol alcohol and benzene. Decomposed by distillation yielding diphenyl, benzene, Ao₂O, HOAo, carbon, and mercury Boiling aqueous HCl forms benzene, HgCl2, and HOAc Other mineral acids act in like manner Sodium amalgam reduces it in alcoholic solution to benzene Iodine, acting on its aqueous solution, forms HgI2, iodo benzene and HOAc H2S forms HgS, benzene, and HOAc

Mercuric phenylo-propionate PhHgOC, H,O [c 166°] From HgPh, and boil ing propionic acid Crystals, sol hot water, alcohol, and benzene

Mercuric phenylo-myristate
PhHgOC₁₄H₂₇O From HgPh₂, myristic acid, and alcohol at 120° Small scales, sol boiling alcohol and benzene Boiling HClAq splits it up into HgCl2, benzene, and myristic acid (Otto, J pr [2] 1, 179).

Mercuric tetra-methyl-di-amido-di-phenyl (NMe, C.H.), Hg [169°] Formed by the action of sodium amalgam in presence of EtOAc on p-bromo-di-methyl-aniline dissolved in xylene (Schenk a Michaelis, B. 21, 1501) Colourless orystalls, turning green in air Crystallises from benzene with C.H. (1 mol.) V e sol chloroform, and benzene, v si sol. alcohol and ether Mercuric di-o-tolyl Hg(C.H.Me), [107°].

From o bromo toluene sodium-amalgam, and

acetic ether (Ladenburg, A 178, 162). Large | or CS2) Not affected by air or light Insol. triclinic tables (from benzene)

Mercuric o-tolylo-chloride
[2 1]C₆H₄Me HgCl o Tolyl-mercuric chloride
[146°] Formed by treating mercuric di o tolyl with HgCl, in ethereal solution (Michaelis a Genzken, A 242, 180) Needles, v sol chloroform, m sol alcohol and benzene, sl sol ether and petroleum ether Sublimes with partial de composition

Mercuric m-tolylo-chloride

[3 1]C₆H₄Me HgCl [160°] Obtained by boiling (C₆H₄Me)₃SbHgCl₂ with alcohol (M a G) Needles (from alcohol), v sol chloroform and benzene, m sol alcohol H₂S passed into its

alcoholic solution ppts HgS

Mercuric di-p tolyl Hg(C,H,Me), [238°] Formed from p bromo toluene, sodium amalgam, and EtOAc (Dreher a Otto, A 154, 171, Ladenburg, A 173, 163) Needles or tables, insol water, sl sol cold alcohol, m sol hot benzene, CS2, and CHCl3 May be distilled Boiling conc HClAq gives toluene and HgCl₂

Mercuric p tolylo chloride

C.H.Me HgCl [187°] Small tables (Otto, J pr

[2] 1, 185)

Mercuric p tolylo rodide C.H.Me HgI [220°] From mercuric di p tolyl and iodine Trimetric satiny tables, insol water, sl sol boiling alcohol, m sol hot benzene May be May be sublimed

Mercuric p tolylo-acetate

C.H.Me HgOAc [153°] Small trimetric prisms, nearly insol cold water, al sol boiling water, m sol alcohol Behaves like the corresponding phenyl compound

Mercuric di-p xylyl (C₆H₃Me₂)₂Hg Prepared by the action of sodium amalgam on bromo p xylene (Jacobsen, B 14, 2112) prisms, sol CS2, chloroform, and benzene, sl sol.

alcohol and ether

Mercuric di-m-xylyl [1 3 4] (C₆H₅Me₂)₂Hg [170°] From bromo m xylene and 2 p c sodium amalgam by heating at 145° for 12 hours (Weller, B 20,1718) Slender felted needles, sl sol ether, alcohol, and cold benzene, v sol hot benzene Boiling HClAq gives HgCl2 and m xylene forms CaHaMeaPCl, (257°) and CaHaMeaHgCl

Mercuric di n-propyl-di phenyl Hg(C,H,Pr)2. [110°] From Br C.H. Pr [14] and sodium-amalgam (R Meyer, J pr [2] 34, 103) Long

ncedles

Mercuric di cymyl Hg(C10H13), Formed by heating a mixture of bromo cymene with xylene and sodium amalgam with addition of a little acetic ether (Paternò a. Colombo, B10, 1749) Long slender needles, m sol boiling alcohol, benzene, and xylene

Mercuric di pentamethyl-phenyl Hg(C_eMe₅)₂. From bromo - pentamethyl - benzene, chloroformic ether, and sodium-amalgam (Jacobsen, B 22, 1220) Prisms (from xylene), v sl sol alcohol and ether, v sol hot xylene

Mercuric di-naphthyl $\operatorname{Hg}(C_{10}H_7)_2$ Mol w [243°] SG 193 (Schröder, B 12, 564) Formed by boiling (a) brome naphthalene with several times its volume of crude xylene, pasty sodium-amalgam, and a little acetic ether for 19 hours, and filtering while hot (Otto a. Möries, A 147, 164, Z [2] 3, 877, 4, 162). Small minute, trimetric prisms (from benzene

water, sl. sol boiling alcohol, cold benzene or ether, m sol hot CS, chloroform, and benzene Decomposed by heat Cone HIAq forms HgI, and naphthalene HCl and HBr act in a similar Iodine forms HgI2, C10H, HgI, and ultimately CleH.I It does not react with HgOl.

Mercuric naphthylo-bronide

 $C_{10}H,HgBr$ [196°] From $Hg(O_{10}H,)_2$ and bromine Formed also by heating $Hg(O_{10}H,)_2$ with $HgBr_2$ Needles, insol water, sol hot alco-

Mercuric naphthylo iodide C19H,HgI [185°] From mercuric di naphthyl and iodine (1 mol) in CS2 Soft sating needles or dendritie Not altered by light, insol water, al sol hot alcohol and benzene Sodium-amalgam converts it into mercuric di naphthyl

Mercuric naphthylo acetate C_{1e}H,HgOAc [154⁵] Formed, together with naphthalene, by heating mercuric di naphthyl with excess of HOAc Small needles (from alcohol), insol water, v sol hot HOAc, alcohol, CS₂, benzene, and chloroform, m sol ether Hot HClAq gives naphthalene and HOAc Sodium amalgam acting on its alcoholic solution forms naphthalene and HOAc Water at 140° has no action

Mercuric naphthylo butyrate C₁₀H, Hg OC₄H,O [200°] Very slender needles, sol hot water

MESACONIC ACID C.H.O. s.c. CH, C(CO.H) CH CO.H Mol w 130 [202°] CH₁ C(CO₂H) CH CO₁H Mol w 130 [202³] 2 6 at 14°, 3 4 at 22° (Baup, A 81, 97) S (90 p c alcohol) 30 6 at 17°, 95 7 at 78° (P), (88 p c alcohol) 38 at 22° (B) R_∞ 46 9 in a 3 69 p c aqueous solution (Kanonnikoff, J pr [2] 31, 349) Heat of solution -5493 Heat of combustion 27,334 (Gal a Werner, Bl [2] 47,159) H C 479,063 (Louguinine, C R 106, 1291)

Formation -1 By boiling a dilute solution of citraconic acid for half an hour with onesixth of its volume of nitric acid Mesaconic acid is deposited on cooling (Gottlieb, A 77, 268, Pebal, A 78, 129, Baup, A 81, 96) -2 By boiling citric acid with cone HIAq or HBrAq (Kekulé, A Suppl 2, 94, Fittig, A 188, 77, 80). 8 By heating a conc aqueous solution of itacome or citracome acid at 180° to 200°, CO, and an empyreumatic oil being also formed (Swarts, Bull Acad. Royale Belgique, [2] 36, No 7) 4 From citra- and mesa di bromo pyrotartario acids by heating with KI and copper at 150° (Swarts, Z 1868, 259)—5 The mono-anilde is heated with (3 mol of) KOH and a little water for 11 hours in the water bath The aniline separates out and is removed by means of ether, the acid being ppd by means of SO_4H_2 (Anschütz, A 254, 136)—6 'Oxy-tetric acid,' which is formed from methyl aceto aceto acid by succes sive treatment with bromine and alcoholic potash (Demarcay, A Ch [5] 20, 473), is identical with mesaconic acid (Gorboff, J R 1887, 605, Cloez,

Bl [3] 3, 598, 602)
Preparation —By evaporating a mixture of citraconic anhydride (10 pts), water (22 pts), and cone HNO_s (8 pts), until red fumes begin to appear The product is crystallised from water (Fittig, A. 188, 73)

Properties - Slender needles (from water) or

prisms (from alcohol), sl sol cold, v sol hot, V sol alcohol and ether May be sublimed without decomposition Its molecular weight, determined by Raoult's method, is identical with that of citraconic and of itaconic acid (Paternò, B 21, 2157) Mesaconic acid is slightly coloured by FeCl₃, and the solution when boiled yields a brown gelatinous pp which re dissolves on cooling The addition of more FeCl, prevents its re dissolving Neutral solutions of mesaconates give a brown pp with FeCl_s, insoluble in excess of the reagent or when

Reactions -1 Conc HIAq at 160° forms pyrotartaric acid —2 Sodium amalgam also re duces it to pyrotartaric acid The same reduc tion may be effected by zinc dust (Bottinger, B 9, 1821) -8 Bromine has no action in the cold (difference from citraconic acid) but above 60° it combines, forming mesa di bromo pyrotartario acid [170°] (Kekulé, A Suppl 2, 85)—4 Chlorme passed into water in which mesaconic acid is suspended forms a solution which when eva porated leaves chloro cutramalic acid C₅H,ClO, (chloro oxy pyrotartaric acid) The same acid is formed, together with tri chloro acetone, by passing chlorine into an aqueous solution of sodium mesaconate -5 Does not combine with HBr in the cold, but by prolonged heating with HBrAq at 100° or 140° it is converted into citra bromo pyrotartaric acid, an acid that is formed also by the union of HBr with citraconic acid in the cold -6 When repeatedly heated with fuming HClAq at 160° it is converted into citra chloro pyrotartaric acid [130°], which is decomposed by boiling water into HCl and mesaconic acid (Swarts) —7 The electrolysis of potassium mesaconate yields, at the positive pole, CO, and allylene (Aarland, J pr [2] 6, 256, 7, 142) – anhydride has not been obtained (Petri, B 14, 1636) - 9 On evaporating a solution of the andine salt water is not eliminated from the molecule (difference from citraconic acid)

Salts -NH,HA" S 125 at 15° Very small prisms -BaA" 4aq monoclinic crystals more sol water than barium citraconate and ıtaconate (Petri, B 14, 1634) —BaH₂A"₂2aq pearly hexagonal plates —CaA"aq S 6 at 20° Very small needles, insol alcohol —PbA" 1 aq deposited in the cold as a crystalline pp, v sl sol water - PbA"aq deposited from a hot solu tion as an amorphous pp —PbH₂A"₂ (dried at 100°) Small needles — (HO Pb)₂A"₂ ppd by adding lead subacetate to a solution of sodium mesaconate (Otto, A 127, 182) — CuA" 2aq — Ag₂A" crystalline pp, sl sol water —AgHA" needles, m sol hot water

Methyl ether Me.A" (205° 1 V) S 8 at $^{\circ}$ S G $^{15}_{1}$ 1 1254, $^{\circ}_{3}$ 1 1138 MM 1 154 at $^{\circ}$ $^{\circ}$ $^{\circ}$ $^{\circ}$ $^{\circ}$ $^{\circ}$ $^{\circ}$ $^{\circ}$ (Gladstone), 1 4570 at 17° (Knops, A 248, 195), $\mu_{\rm H}$ 14813 at 16° (Gladstone) From the acid, MeOH, and HCl (Perkin, C J 39, 556)

Ethyl ether (229° 1 V) SG 15 1051, 20 1089 (Perkin), 20 10468 (Knops, A 248, 196) MM 1168 at 25° μ_D 14483, μ_R 14727 at 16° (Gladstone, cf Knops) Formed by the action of alcohol and HCl on mesaconic and on sitraconic acids

Chloride C₂H₄(COCl)₂ (80° at 17 mm).

Prepared by the action of PCl, on mesaconic acid or citraconic anhydride (Petri, B 14, 1634). Colourless liquid

 $Amide C_3H_4O_2(NH_2)_2$: [177°], colourless

flat crystals, sol water

Anilide C,H,O,(NHPh)₂ [186°], flat white
sliky needles, sol alcohol and ether, sl sol Heated to 268° it decomposes into aniline and citraconenil (the phenylimide of citraconic acid) (O Strecker, B 15, 1639)

Mono anilide C₃H₄(CO₂H)(CONHPh). [158°] Formed by heating citraconic anhydride with aniline at 170°, rectifying in vacuo the re sulting phenylimide (172° at 12 mm), dissolving it in baryta water, ppg excess of barium by CO, and then adding HCl (Anschutz, A 254, 133). Identical with the product which separates from an aqueous solution of acid aniline citraconate White powder on standing Converted by heating in a sealed tube with KOH into mesaconic acid

Constitution - Mesaconic acid stands to citra conic acid in the same relation that fumaric stands to maleic acid This is shown by their behaviour towards Br, HBr, and aniline, and by the physical constants of their ethers Hence mesaconic acid is methyl fumaric acid, while citraconic acid is methyl makic acid The constitution of mesaconic acid will there fore be known as soon as that of fumaric acid has been satisfactorily determined (v Maleic

MESA-DI BROMO PYROTARTARIC ACID v. DI BROMO PYROTARTARIC ACID

TRIMESIC ACID C,H,O, 1 e

 $C_bH_3(CO_2H)_3[1\ 3\ 5]$ Benzene s tri carboxylic 0 [c 325°] HCv 768,500 HF 285,400 (Stohmann, acid Mol w 210 HCp 767,600 Kleber & Langbein, J pr [2] 40, 140)

Formation -1 By the oxidation of mesi tylene or mesitylenic acid by chromic acid mix ture (Fittig, A 141, 153) -2 By the oxidation of uvitic acid (Baeyer, Z 1868, 119, Fittig, A 147, 301), and of s tri ethyl benzene (Jacobsen, B 7, 1435, Friedel a Balsohn, Bl [2] 34, 636) by chromic acid mixture -3 One of the pro ducts obtained by heating hydromellitic or iso hydromellitic acid with cone H2SO4 (Baeyer, A Suppl 7, 40, 48) —4 By heating mellitic acid with glycerin (Baeyer, A 166, 340) —5 In very small quantity by fusing the corresponding bromo benzene sulphonic acid with sodium formate (Bottinger, B 7, 1781) -6 By fusing benzene s trisulphonic acid with KCy, and sa ponifying the resulting nitrile with KOH (Jack son a Wing, Am 9, 347) -7 From di sodium salicylate C,H,(ONa) CO,Na by heating in a cur rent of carbonic acid, converting the resulting C_bH₂(OH)(CO₂H)₃ into C_sH₂Cl(CO₂H)₃, and re ducing with zinc and dilute acids —8 By the polymerisation of propiolic acid, which takes place to some extent when it is exposed for some weeks to sunlight, air being excluded (Baeyer, B 19, 2185) -9 Trimesic ether is formed by the action of sodium upon a mixture of ethyl formate and ethyl acetate, formyl acetic ether HCO CH2 CO2Et is probably first formed and subsequently condensed (Piutti, B 20, 537) When mixtures of methyl formate and ethyl acetate. or of ethyl formate with methyl acetate

are used a mixture of ethyl and methyl trime sates is obtained

Properties - Colourless prisms (from water) partially sublimes before melting M sol cold water and ether, v sol hot water, v e sol When distilled with lime it yields benzene

Salts —NaH,A" plates, sl sol cold water —Na,A" —KH₂A'" needles, sl sol cold water — Ca,A",2q nodules — Ba,A",aq (dried at 150°) needles, almost insol cold, v sl sol boiling (difference from mesitylenic acid) -BaH₄A'''₂4aq slenuer hair like needles, sl sol cold water — Zn₃A'''₂2aq glittering prisms, almost insol cold water — Cu₃A'''₂aq (dried over H₂SO₄) Pale blue pp —Ag₂A''

Methyl ether Me₃A''' [143'] Small silky

needles HF 249,500 (Stohmann, J pr [2] 40,

Ethyl ether Et,A" [133°] Prepared by adding a mixture of formic and acetic ethers by drops to twice the amount of ether, in which sodium is placed. On adding dilute H SO, an oil is obtained, which gives a blue violet colour with FcCl3, and on standing in a desiccator de posits crystals of trimesic ether (Wislicenus, B 20, 2930) Long glistening prisms A mixture of this ether and the preceding in equal propor tions melts at 105° to 110°

Sulpho trimesic acid Amide

CoH2(SO NH2)(CO2H)3 Formed by oxidising the amide of either of the sulpho mesitylenic acids with KMnO, (Jacobsen, A 206, kH₂A''' 2aq crystalline mass, m sol water Conc HClAq at 210° gives trimesic acid, NH₃, and $\rm H_2SO_4$ Potash fusion gives oxy trimesic **sc**id

MESICERIN v TRI OXY MI SITYLENE MESIDIC ACID v UVITIC ACID MESIDINE C9H13N 1e

 $C_bH_a(CH_a)_sNH$, [1 3 5 6] Amido mesitylene (229°) (Ladenburg, A 179, 172) SG 963

Formation -1 By boiling nitro mesitylene with tin and HClAq (Fittig a Storer, A 147, 1) -2 From di methyl aniline methylo iodide, by heating in a sealed tube at 335° (Hofmann, B 5, 715, 8, 61) -3 By heating u m xylidine hydrochloride or c m xylidine hydrochloride with methyl alcohol at 300° (Eisenberg, B 15, 1012, Nolting a Forel, B 18, 2681) -4 By heating aniline hydrochloride with MeOH at 300° (Lim pach, B 21, 640)

Properties - Liquid Gives m xyloguinone on oxidation When heated with MeOH and HCl for forty eight hours at 230° it yields dimethyl mesidine (c 215°) ClCO Et yields C_sH Me₃ NH CO₂Et[62°] (Eisenberg, B 15,1016)

Salts -B'HCl feathery crystals or prisms, ▼ sol water and alcohol - B' H,SnCl, ingly soluble needles -B'2H2PtCl5 -B'2H2C1O4 plates, sl sol cold water

C₆H₂(CH₃)₃NHAc Acetyl derivative [217°] Prisms (from alcohol) May be sublimed C₆H₂(CH₃)₃NHBz

Bensoyl derivative C.H. (CH [204°] Needles (Schack, B 10, 1711)

MESIDINE SULPHONIC ACID C.H., NSO. nesstylene sulphonic acid From nitro mesitylene sulphonic acid by reduction with NH2 and H.S (Rose, A 164, 70) Slender prisms or needles (containing aq) (from water), v sol. hot

alcohol, sl sol cold water Does not combine with HCl or H_2SO_4 —BaA'₂ nodules, m sol cold water—MgA'₂ Saq—ZnA'₂ 5aq—PbA'₂aq . crystalline, v sol cold water—AgA'

MESITENE LACTONE v vol 1 p 21 and Bromo mesitene lactone

TRI-MESITIC ACID v PYRIDINE TRI CARB OXYLIC ACID

MESITOL C.H.2O re

C₀H₂(CH₃)₃(OH) [1 3 5 6] Oxy mesitylene [69°] (219 5° 1 V) Obtained from mesidene by the diazo reaction, and by fusing mesitylene sulphonic acid with potash (Biedermann a Ledoux, B 8, 57, 250, Jacobsen, A 195, 268) Crystals, v e sol alcohol and ether Volatile with steam Insol NH, Aq and aqueous Na₂CO₃, v sol NaOHAq Not coloured by FeCl₃ Forms a sulphonic acid, which has an easily soluble barium salt, coloured deeply by FeCl, This sul phonic acid yields oxy mesitylenic acid by potash fusion

Methyl derivative C.H. (CH3)3(OCH3) (c 202°) Liquid Bromine gives a bromo derivative [80°] V Amido- and Bromo mesitol

MESITONIC ACID C H12O, or (CH₃)₂C(CO₂H) CH₂CO CH₃(?) Di a methyl B acetyl propionic acid [74°] (Anschutz) [90°] (P) (138° at 15 mm) (230°-240°) at 760 mm Prépared, together with an acid (C.HisNOs) and phoronic nitrile (C₁₁H₁₈N₂O₂), by boiling the pro duct of the action of gaseous HCl on acetone, with alcoholic KCN In this reaction the sub stance first formed is probably the chloride (CH₃) CCl CH CO CH₃, which by KCN would give the nitrile of mesitonic acid (Pinner, B 14, 1071) Plates or prisms Sol water, alcohol, ether, and benzene, sl sol petroleum ether Its salts are v e sol water On distillation it splits off water, forming mesito lactone C, H, O2. Yields di methyl malonic acid on oxidation with HNO, (Anschutz, A 247, 103) On reduction it yields the lactone of γ oxy di a methyl-valeric acid (CH_s)₂C CH_xCHMe O CO [52°]

Ethyl ether C.H10(OH) CO2Et (210°) Colourless liquid

Acetyl derivative of the ethyl ether C_sH₁₀(OAc) CO I t (206°) Liquid (Pinner, B 15, 578)

Phenyl hydrazide

PhHN, CMe CH CMe, CO.H [121 5°] prisms (from benzene or dilute alcohol) On boiling with a few drops of HClAq it yields crystalline C₁₃H₁₆N₂O [84°]

Compound with Hydrogen Cyanide C₃H₁₃NO₃ is CH₃ C-CH₂-CC_{CO₂H}.

- NH

Mesitylic acid [174°] Prepared, together with mesitonic acid and phoronic nitrile, by boiling the product of the action of HCl on acetone with alcoholic KCN In this reaction it is probably formed by the addition of HCN to mesitonic acid or its nitrile (Simpson, A 148, 351, Pinner, B 14, 1071, 15, 580) Distils undecomposed at a high temperature Large flat prisms (containing aq) Very stable body Forms easily soluble salts By heating with HCl to 140° CO₂ and NH₃ are split off Heated with concentrated H₂SO₄ to 150° it is converted into mesitonic acid On oxidation with KMnO. in acid solution it gives di methyl succinimide and di-methyl malonamic acid [107°]

Ethyl ether A'Et [90°] Colourless prisms Sol alcohol and in acid, sl sol water Amide C₈H₁₄N₂O₂ [222°] tals Sol water and alcohol Colourless crys-

Mesito lactone C7H10O2 te (CH₃)₂.C CH C CH₃

Lactone of Oxy heptenoic ¢0--0

(167°)Prepared by distillation [24°] acid of mesitonic acid (Pinner, B 15, 579) Large colourless prisms, sl sol water Neutral body By boiling with KOH it is reconverted into mesitonic acid It combines with bromine

MESITYL This name was given by Kane (P 44, 476) to a radicle C, H, of which he supposed acetone to be the hydroxide and Mesityl oxide $(q \ v)$ the oxide More recently it has been employed to denote both s di methylbenzyl and s tri methyl phenyl

MESITYL ALCOHOL υ ω ΟΧΥ ΜΕSITYLENE

MESITYL BROMIDE v BROMO MESITYLFNE MESITYLENE C₉H₁₂ re C₆H₃Me₃ [1 3 5] 'rr-methyl benzene Mol w 120 (164 5°) *-Tri-methyl benzene (Schiff, A 220, 94) S G $\frac{98}{4}$ 8694 (S), $\frac{20}{4}$ 8558 (Bruhl, A 200, 190) C E (98° to 1645°) (Schiff, A 200, 190) CE (98° to 1645°) 001159 (S) VD 44 (obs and calc) SV 1624 (Schiff), 1622 (Runsvy) $\mu_{\beta} = 15015$ $R_{\infty} = 6575$ (B) H C = 1,251,660 [C,O₂ = 94,000, H₂O = 69,000] (Stohmann, J pr [2] 35, 41), 1,282,310 (Thomsen, Th 4, 63) H F p = 490 H F v = -2410 (Th)

Occurs in coal tar oil (Fittig a Wackenroder, A 151, 292, Jacobsen, A 184, 179, B 9, 256, 10, 855) It is also one of the products of the manufacture of oil gas (Armstrong, C J 49, 74) Occurs in all kinds of petroleum (American, Russian, &c) (Engler, B 18, 2234)

Formation -1 By distilling acetone with H,SO₄ (Kane, P 44, 474, Hofmann, C J 2, 101, Cahours, C R 24, 255, C J 3, 17) — 2 By the action of H_2SO_4 on allylene (Fittig a Schrohe, B 8, 17) -3 By treating toluene with MeCl in presence of AlCl, y cumene being also formed (Friedel a Crafts, A Ch [6] 1, 461,

Ador a Rilliet, B 12, 329)

Preparation -1 By mixing 180 g acetone with 300 g sulphuric acid, allowing to stand for an hour, then distilling gently, using a current of steam at the end of the operation The yield is 40 g (Varenne, Bl [2] 40, 266) -2 H₂SO₄ (2 vols) diluted with water (1 vol) is slowly added to a mixture of crude acetone (2 vols) and sand After 24 hours the mixture is distilled The oil thus obtained is washed with aqueous NaOH and rectified (Fittig a Bruckner, A 147, 42) -8 The fraction of coal tar oil boiling between 160° and 168° is agitated with H2SO4 and the resulting sulphonic acids converted first into Ba salts and then into Na salts The Na salts are then treated with PCls, and the resulting chlorides converted into amides by NH₃Aq . On crystallising from alcohol, the v cumene sulphonamide separates first, and then mesitylene sulphonamide The mesitylene sulphonamide is then heated with cone HClAq at 160° (Jacob sen) -4 The sulphonic acids of ψ cumene and of mesitylene may also be separated by heating

with HClAq at 100° for 1 hour, when mesitylene sulphonic acid is decomposed into mesitylene and H,SO, while ψ cumene sulphonic acid is not affected (Armstrong, B 11, 1697) -5 When steam is passed through a heated solution of mesitylene sulphonic acid in dilute H2SO4, hydrolysis into mesitylene and H,SO, begins as soon as the temperature reaches 100° (Armstrong a Miller, \hat{C} J 45, 148)

Properties —Light oil
Reactions —1 Br and Cl form crystalline substitution products -2 Fuming HNO3 mixed with fuming H₂SO, forms 4ri nitro mesitylene. 3 Boiling dilute HNO₃ oxidises it to mesitylenic acid and uvitic acid (Fittig, A 141, 142) — 4 K₂Cr₂O, and H₂SO₄ yield acetic acid (Fittig) 5 KMnO, oxidises it to uvitic and trimesic acids (Jacobsen, A 184, 191) -6 When heated with AlCl, in a current of HCl it yields MeCl and m xylene, toluene, and benzene (Jacobsen, B 18, m xylene, toluene, and behinden (Jacobsen, B 13, 342) -7 MeI in presence of AlCl, yields (1, 2, 4, 5) tetra-methyl benzene (durene) (Barbier a Roux, Bl [3] 2, 4) -8 Benzyl chloride and AlCl, at 100° form benzyl mesitylene (q v) 9 Benzoyl chloride in presence of aluminium chloride forms phenyl tri methyl phenyl ketone C_sH₃ CO C_sH Me, [36°] and the compounds (C_sH₃ CO)₂C_sHMe, [117°] and (C_sH₃CO)₃C_sMe, [215°] (Louise, A Ch [6] 6, 200) —10 PCl, at 180° gives a small quantity of C_sH₃(CH₂Cl)₃ (Colson a Gautier, Bi [2] 45, 6) —11 Mestylene is very readily attacked by halogens In the dark, mono- di- or tr. (eso) bromo mesitylene (C₆H₂Me₃Br, C₆HMe₃Br, and C₆Me₃Br₃) are formed according as 1, 2, or 3 mols of bromine are em ployed Chlorine acts similarly The presence of iodine, though not required, does not effect At the boiling point the bromine, the reaction as usual, enters the side chains, 1 mol Br forming ω bromo mesitylene (mesityl bromide) C_e(CH_s)₂CH₂Br melting at [38°] Direct sun shine, which usually acts like heat, in the case of mesitylene, owing to the great tendency to dis placement of the nucleal hydrogen, produces a different result, (eso) mono brome mesitylene is first produced but is partly attacked by the rest of the bromine forming the liquid $p \propto di$ bromo mesitylene (p bromo mesityl bromide) C₆H₂(CH₃),Br(CH₂Br) [5 3 4 1] If eso bromo mesitylene be exposed to further bromination in sunshine, the reaction proceeds normally, pioducing $p \omega$ di bromo mesitylene (as above), and, on further action, $p \omega_1 - \omega_2$ tri bromo mesitylene $C_0H_2(CH_3)Br(CH_2Br)$, [5 4 3 1] melting at [122°] (Schramm, B 19, 212) —12 When a 10 pc solution of mesitylene in CS2 is mixed with a similar solution of chromyl chloride CrO, Cl, a pp (C,H3Me2)(CrO2Cl2) is obtained which when decomposed by water yields dimethyl benzoic aldehyde (221°), which is oxidised by air to mesitylenic acid (Etard, C R 97, 909) —13 The diacetyl derivative of ortho formic aldehyde (1 pt) mixed with mesitylene (1 pt) and HOAc (10 pts) condenses on adding a mixture of HOAc (10 pts) with an equal volume of H₂SO₄, and after 24 hours crystals of (O₆H₂Me_{s/2}CH₂ [130°] separate The formation of this body may be used as a test for mesitylene, a mixture of methyl alcohol and CrO, in HOAc being used instead of CH₂(OAc)₂ (Baeyer, B 5, 1094, 6, 220)

Constitution.—The explanation of the for.

mation of mesitylene by condensation of acetone was first given by Baeyer (A 140, 306) That the three methyls are symmetrically situated in the benzene nucleus would appear from the existence of only one mono-derivative derived by displacing an atom of hydrogen in the nucleus, eg there is only one nitro mesitylene A systematic proof of the symmetry of mesitylene has been given by Ladenburg (A 179, 163) He prepares in succession C₆Me₂(NO₂)(NO₂)H, C₆Me₃(NO₃)(NH₂)H, C₆Me₃(NO₃)(NH₂)(NO₂), and C₆Me₃(NO₂)H(NO₂) Since the last dinitromesitylene is identical with the first, the second and third hydrogen atoms are similarly situated in the nucleus Again, from the above nitro in the nucleus Again, from the above nuro mesidine $C_8Me_s(NO_s)(NH_s)H$ Ladenburg obtained $C_8Me_s(NO_s)HH$ and, by reducing this, mesidine $C_8Me_s(NH_s)HH$ Nitro mesidine, obtained by nitrating $C_8Me_s(NH_s)HH$, must be either $C_8Me_s(NH_s)(NO_s)H$ or $C_8Me_s(NH_s)H(NO_s)$ But since it has been shown that the second and third storms of hydrogen are similarly situated third atoms of hydrogen are similarly situated, these two formulæ are identical And since the nitro mesidine is found to be identical with the C₈Me₃(NO₂)(NH₂)H prepared from the dintro mostylene C₈Me₃(NO₂)(NO₂)H, it follows that the first and recond atoms of hydrogen are similarly situated Hence all three atoms of hydrogen are similarly situated, and the formula will be C.Me.H. [1 3 5]

Mesitylene hexahydride C,H18 2 C C6Me1H Obtained by heating mesitylene with PH I at 280° (Baeyer, Z [2] 5, 320, A 155, 273) Oil, smelling like petroleum Converted by pro longed heating with fuming HNO, into tri nitro

mesitylene

References -- DI AMIDO, BENZYL, BROMO, BROMO NITRO, BROMO OXY, CHLORO, DI CHLORO BROMO-, CHLORO NITRO , NITRO-, NITRO BI VZYI , DI OXY- and TRI OXY MESITYLENE V also V also MESIDINE, MESITOL, and AZO COMPOUNDS

MESITYLENE-DIAMINE v DI AMIDO MESI TYLENE, vol 1 p 166
MESITYLENE CARBOXYLIC ACID v (8)-

Iso cuminic acid

MESITYLENE GLYCOL v DI ONY MESITYL-

MESITYLENE PHTHALOYLIC ACID v PHENYL TRI METHYL PHENYL KRYONF CARBOXYIIC

MESITYLENE SULPHINIC ACID

[99°] $C_6H_2Me_3SO_2H$ [1 3 5 6] Formed by adding a mixture of sodium amalgam and C.H.Ne.SO,Cl to a dry mixture of benzene and toluene, and decomposing the resulting pulpy mass with HCl (Holtmeyer, Z 1867, 686) shaped groups of needles —BaA', raq —AgA'
MESITYLENE SULPHONIC ACID C,H,2SO,

te C₆H₂Me₃SO₃H [c 77°] Formed by dissolving mesitylene in warm H, SO, (Hofmann, C J 2, 113, Jacobsen, A 146, 85, 184, 185, Beilstein a Kögler, A 137, 317, Fittig, J 1866, 610, Z [2] 4, 583) Trimetric six sided tables (containing 2aq) (Rose, Z [2] 6, 341, A 164, 53, Bodewig, J 1879, 737) Decomposed by distillation with dilute H₂SO₄ into mesitylene and H_2SO_4 , the hydrolysis beginning at 100° (Armstrong a Miller, C J 45, 148). Gives mesitol on potash-fusion (Jacobsen, A 195,

Salts.-KA'aq. Roundish groups of silky

S 14 at 12° -NH, A' aq laminæ Plates, v sol water and alcohol -- CaA' 25aq efflorescent crystals —BaA'₂ 9aq S 6 6 at 18°, 5 5 at 11 5° —SrA'₂ 7aq —MgA'₂6aq —CoA'₂6aq flesh coloured laminæ, v. sol water and alcohol. CuA'₂4aq Pale green laminæ S 6 s bA'₂9aq Pearly plates S 15 at 20° Chloride C₈H₂Me₈SO₂Cl [57°] Pale green laminæ S 6 at 10°.-PbA', 9aq

Wedgeshaped tables (from ether), insol water, v sol alcohol and ether (Holtmeyer, Z 1867, 686)

Amade C.H.Me. SO. NH. [142°] S 033 at 0°, 54 at 100° S (83 p c alcohol) 55 at 0°, 114 at 78° Fibrous mass (from alcohol) or hair like needles (from ether) May be oxidised to $C_6H_2Me(CO_2H)_2SO_3NH_2$ and an acid $C_6H_2Me_2(CO_2H) SO_2NH_2$, and the anhydride of

an isomeric acid $C_0H_2Me_2 < SO_2 > NH$ (Hall a.

Remsen, Am 2, 130, Emerson, Am 8, 268)

Imide (C.H.Me.SO.). HH [124] Formed by heating the amide with a little HCl in a sealed tube Long needles, m sol hot water, sol

NaOHAq, and reppd by HCl

Mesitylene disulphonic acid C.HMe2(SO.H), Formed by dissolving mesitylene (1 pt) in fuming H₂SO₄ (10 pts) and adding P₂O₅ (3 pts), the temperature being kept low during the opera-tion (Barth a Herzig, M 1, 807) Deliquescent needles Gives oxy mesitylenic acid on potash fusion — K₂A" 2aq — Na₂A" 1½aq needles — BaA" 3aq needles — CuA" (dried over H₂SO₄) greenish white needles

Reference - Bromo - MESITYLENE SULPHONIO

MESITYLENIC ACID C, H10O2 te

C₆H₃Me₂CO H Di methyl benzoic acid Mol [166°] H C v 1,084,300 H C p H F 105,800 (Stohmann, Kleber, a 150 1,085,200 Langbein, J pr [2] 40, 135) Colourless plates

Formation -1 By boiling mesitylene with dilute HNOs (1 vol of SG 14 and 2 vols water) The product is distilled with for 18 hours steam, boiled with a little tin and HClAq to re move a nitro compound, and crystallised from alcohol (Fittig, A 141, 144, Fittig a Brückner, Z [2] 4, 493, A 147, 45) -2 By boiling s dimethyl ethyl-benzene with mirro acid (S G 11) (Jacobsen, B 7, 1430, Wroblewsky, B 9, 495) 3 By passing CO over a mixture of NaOEt and NaOAc at 205°, or by heating such a mixture with zinc dust (Geuther a Fröhlich, A 202, 310)

Properties — Monoclinic crystals (from alcohol), v sl sol water, v sol alcohol Sublimes below its melting point Distillation with lime yields m xylene Chromic acid mixture oxidises

it to trimesic acid

Salts —NaA' (dried at 130°) V sol water and alcohol —CaA', and Not more soluble in hot than cold water - BaA', silky priems -MgA', 5aq groups of monoclinic prisms -ZnA'₂ (dried at 130°) laminæ or needles, sl sol water —MnA'₂.—NnA'₂ (dried at 130°) —AgA'₂ Minute needles, sol hot water —AgA'₂ aq (Hall a Remsen, Am 2, 130)

Ethyl ether EtA' (241°) Heavy oil;

solidifies below 0°

Amide C.H.Me, CONH, [133°]. Needles;

v. sl sol cold water References - AMIDO- BROMO-, and CHLORO-MESITYLENIC ACID.

MESITYLENIC GLYCOL v DI OXY MESITYL

MESITYLENIC GLYCERIN v TRI-OXY ME SITYLENE

MESITYLIC ACID v compound of MESITONIC ACID With HCy

MESITYL MERCAPTAN v. TRI-METHYL-PHENYL MERCAPTAN

MESITYL OXIDE C.H., O i e (CH.), C CH CO CH. Methyl isobutenyl ketone Isopropylidene acetone (132°) at 751 mm $8 \ G^{-\frac{30}{4}} 8578 \ \mu_D \ 14440 \ V \ D \ 3 \ 67 \ (calc \ 3 \ 39)$ R_ω 49 7 (Kanonnikoff, J pr [2] 31,852)

Formation —1 One of the products of the

action of H.SO, on acctone (Kane, P 44, 476) 2 Together with phorone by leaving acctone for several weeks in contact with quicklime (Fittig, A 110, 32) -3 One of the products of the action of ZnEt₂ or ZnMe₂ on acetone (Pawlow, B 9, 1311, A 188, 130)—4 In small quantity, together with other bases, by distilling diaceton amine (Heintz, A 174, 133, 181, 70, B 8, 89) -5 By boiling with lime the lactoric products of condensation of aceto acetic ether (Hantsch, A 222, 21) -6 By boiling acetyl chloride with acetone (Beilstein a Wiegand, Bl [2] 38, 167) -7 Among the products of the dis tillation of glycerin with BaO (Destrem, A Ch [5] 27, 5)

Preparation —Acetone is saturated with HCl and then left to itself for a fortnight The pro duct is mixed with water, and the heavy oil, con taining hydrochlorides of mesityl oxide and phorone, decomposed by alcoholic or cone aqueous KOH, and distilled with steam The product is fractionally distilled (Baeyer, A 140,

Properties -Oil, smelling like peppermint, insol water, miscible with alcohol and ether

Reactions —1 Boiling dilute sulphuric acid forms acetone Cone H₂80, gives mesitylene (Claisen, B 7, 1168) —2 Boiling dilute nitric acid yields acetic and oxalic acids -3 KMnO. oxidises it to acetic and oxy isobutyric acid (Pinoxidases it to acetic and oxy isobutyric acid (Pinner, B 15, 591)—4 Slowly combines with NaHSO, forming NaC₆H₁₁SO₄aq, the sodium salt of methyl isobutyl ketone sulphonic acid CH₂ CO CH₂ CMe₂ SO₂H, which is decomposed by cone NaOHAq regenerating mentyl oxide (Pinner, B 16, 1727)—5 Bromme acts violently But when it is added to a solution of mesityl oxide in CS2 oily C6H10Br2O is formed This can be distilled with steam, but in the dry state soon gives off HBr -6 A solution in dilute alcohol is strongly attacked by sodium amalgain and water then ppts a heavy oil $C_{12}H_{20}O$ 'mesitic ether' or 'mesitic camphor' (c 215°) smelling like camphor A small quantity of a solid [110°-120°] is also formed (Claisen, A 180, 7) -7 PCl, forms 'mesityl chloride' C,H10Cl2, which separates on adding water as a heavy oil, smelling like oil of turpentine It resinifies on exposure to air, and is decomposed by distillation over KOH, baryta, or lime into HCl and C₆H₉Cl, a liquid (130°) smelling like turpentine 8. Ammonia forms diacetonamine C.H., NO — 9 Hydriodic acid forms a heavy oil C.H., IO decomposed by alcoholic KOH into HI and mesitylene (Pawlow, A 188, 188) —10 HCl passed into a mixture of mesitylene and benzoic aldehyde forms C.H. CO CH CHPh (Classen a.

Claparède, B 14, 849) -11 With acetamide and ZnCl₂ it forms oxy-tri methyl pyridine di hydride (Canzoneri a Spica, G 14, 349, B 19, 818, cf Engler a Riehm, B 19, 40) —12 With amyl nitrite and alcoholic NaOEt it forms the nitroso- derivative CMe, CH CO CH NOH, crys tallising in colcurless prisms [102°] (Claisen a Manasse, B 22, 529)

Oxim C₆H₁₁NO i e (CH₃),C CH C(N OH) CH₃ (c 185°) Formed by the action of hydroxylamine on mesityl oxide (Nageli, B 16, 495) Oil Sol alcohol, ether, benzene, CS, ligroin, alkalis and acids On warming with acids it is resolved into its con stituents

MESOCALIPHORIC ACID v CAMPHORIC ACID MESORCIN v TRI-METHYL RESORCIN

MESOTARTARIC ACID v TARTARIO ACID

MESOXALIC ACID C₈H₂O₅aq 1 e CO,H CO CO,H+aq or CO,H C(OH), CO H (Petrieff, B 11, 414) Mol w 136 [115°] (Petrieff, B 11, 414) Mol w 136 [115°] (Deichsel), [108°] (Böttinger, A 203, 140), [120°] (Fischer)

Formation —1 Together with urea, by ing alloxan or alloxanic acid with baryta -1 Together with urea, by boil resulting Ba salt is recrystallised and decom posed by H.SO, (Liebig a Wohler, A 26, 298, Svanberg, B J 27, 165, Deichsel, B B 1864, 587) -2 By treating amido malonic acid with iodine and water (Baeyer, A 131, 298) -3 By boiling di bromo malonamide CBi (CO NH2), with precipitated Ag₂O (Freund, B 17, 782) —4 By boiling di bromo malonic acid with baryta water (Petrieff, J. R. 10, 72) -5 By heating caffuric acid with concentrated aqueous lead subacetate (E. Fischer, A. 215, 283)

Properties - Very deliquescent prisms, melt ing without loss of aq M sol alcohol and ether, v e sol water Its concentrated aqueous solution decomposes above 80° into CO2, gly collic, oxalic, and glyoxylic acid (Bottinger, A 203, 138) With acetates of Ba and Pb it gives flocculent pps gradually becoming crys talline In neutral solutions CaCl, and BaCl, give pps It reduces hot ammoniacal AgNO,

Reactions -1 H.S passed into an aqueous solution to which silver oxide has been added forms thio glycollio acid CH2(SH) CO2H and thio di glycollic acid (sulphido diacetic acid) S(CH₂ CO₂H)₂ (Bottinger) -2 Sodrum amalgam acting on its dilute aqueous solution forms tar tronic acid CO₂H CH(OH) CO₂H - 3 Silver mes oxalate boiled with water yields CO₂, oxalio and, and silver —4 Urea at 100° gives allantom C₄H₆N₄O₃ —5 Hydroxylamine yields the oxim which is identical with nitroso malonic acid

Salts — [A" = C,O,] — (NH,),A" granular crystals turning red in air (Deichsel, cf Engel, C R 98, 628) -(NH,), A"aq Obtained by evaporation in vacuo over H₂SO₄—Needles (Petrieff)—Na₂A"aq thin laminæ, v sol water—CaA"aq white pp insol dilute acetic acid—CaA"4aq (dried at 100°) (Petrieff)—BaA"aq (dried at 110°). White crystalline powder, v sl sol water—BaA"1½aq—BaA" (dried at 180°)—(HO Pb)₂A" nearly insol water —Ag₂A"aq amorphous pp changing to minute needles Explodes when heated

Ethyl ether Et. A"aq. From the silversalt and EtI. Oil.

D: acetyl derivative of the ethyl ether (CO₂Et)₂C(OAo)₂ [145°] From the ether (1 mol) and AcOl (2 mols) at 100° (P) Long needles Partially decomposed by fusion and by solution in water

Dr acetyl derivative C(OAc),(CO₂H)₂ [180°] From (CO₂Et)₂C(OAc)₂ and dilute alcoholo KOH Needles Its alkaline salts are v sol water, its silver salt Ag₂C,H₈O₈ is an insoluble powder

Amide C(OH)2(CONH2)2. Deliquescent

tables, which turn red in the air

Phenyl-hydrasıds PhHN₂C(CO₂H)₂ [158°-164°] From mesoxalıo acıd and phenyl hydrazıne hydrochloride in dilute acid solution (Elbers, **A** 227, 355)

Phenyl hydraside of the Nitrile
PhHN₂ C(CN)₂ [135°] May be formed from
the oxim phenyl hydrazide of glyoxylyl cyanide
HO N CH C(N₂HPh) CN by dissolving in POCl₃,
heating with PCl₃, pouring into ice, and treating
the crystals with ether and alkali (Von Pech
mann a Wehsarg, B 21, 3001) Yellow needles
(from ether ligroin) Turns brown at 126°
Sol hot water, alkalis, and the usual menstrus
Conc H₂SO₄ forms a blood red solution net
changed by FeCl₂ On warming with conc
HClAq it forms yellow needles of C₅H₈N₄O
[215°.

MESOXALIC ALDEHYDE CHO CO CHO
Oxim HON CH CO CH NOH or

ON CH CO CH₂ NO v DI NITROSO ACETONE

Mesoxalic semi aldehyde *CHO CO CO₂H Glyoxylyl carboxylic acid

Diphenyl hydraside

CH(N,HPh) C(N,HPh) CO,H [203°] From dibromo pyruvic acid in aqueous solution and phenyl hydrazine hydrochloride (Nastvogel, A 248, 87) Reddish yellow needles (from hot alcohol), almost insol water, sl sol ether and chloroform, v sol hot alcohol, acetone, benzene and HOAc Dyes wool and silk yellow Cold cone H₂SO₄ forms a dark red solution from which it is ppd by water unaltered

Dip tolyl hydrazide CH(N₂HC₆H₄Me) C(N₂HC₆H₄Me) CO₂H [188°] Formed in like manner Golden needles (from benzene) Its alkaline salts are v sol hot, sl sol cold, water

Nitrile *CHO CO CN v Glyoxylyl

cyanide

Mesoxalic bromo semi aldehyde

™CBrO CO CO₂H

Methyl ether of the oxim
CBiO C(NOH) CO₂Me [c 170°] From dimethyl di bromo pyrrole di carboxylate and
HNO, at -18° (Ciamician a Silber, B 20,
2601) Crystalline, sol alcohol, m sol cold
water, insol petroleum ether Decomposed by
fusion and by boiling with water

MESOXALYL-UREA IS ALLOXAN See also its compounds with METHYL ANILINE, NAPHTHYL

AMINE, and PYRROLE

META Use of this prefix applied to mor game compounds, for Meta-acids and Meta salts with a solds or salts to the name of which Meta-is prefixed. Thus Meta-phosphoruc acid will be found under Phosphoruc acids, and Meta stannates under stannates, a subdivision of the artials Tre.

Names of organic bodies beginning with 'meta' will be found under the word to which 'meta' is prefixed

METACETONE The mixture obtained by distilling sugar with quicklime, called metacetone by Fremy (A Ch [2] 59,6), is composed according to E Fischer a Laycock (B 22, 101) of propionic aldehyde, di methyl-furfurane, and hydrocarbons

METACETONIC ACID An old name for

Propionic acid

METALBUMIN v PROTEIDS, Appendix C METALDEHYDE v Aldehyde

METALLIC ACIDS In the article Acids (vol 1 p 47, cf Classification, vol 11 pp 201, 202), it is shown that compounds of H with certain negative elements or groups of elements react with metallic oxides, hydroxides, and car bonates, in presence of water, to produce sub stances composed of metal, and the elements of the hydrogen compound excepting the H or a part of the H Such hydrogen compounds are The negative elements which are called acids found intimately combined with H in acids are fluorine, chlorine, bromine, iodine, oxygen, sul phur, selenion, tellurium, carbon always enters into the composition of those negative groups of elements which combine with H or with H and other elements to form acids Only a few acids are binary compounds, the greater number are compounds of H with two or three other elements, among which are always found at least one of the eight negative elements enumerated above, or at least one of the negative carbon containing groups of elements By far the greater number of the more stable and definite acids are com posed of H combined with non metallicelements, but some acids have been isolated which are composed of H combined with metals and one or more of the eight strongly negative elements already enumerated, or one or more of the car bon containing negative groups of elements The following table gives the composition of most of those acids which contain metallic elements -

Metallic acids H,AsO, (?H₂T₁O₂) (?H₄T₁O₄) H_PtCy_Cl_ H,PtBr. HAsO, H.Pt.S. H2SnO H,As,O, H2Sn2O. H₄OsCy₄ (?H_sAsS₄) H,SnS, H.RuCy. H,IrCy, H,SbO. (?H,PbO.) H PbI, HaNgOs,O HSbO, H,Sb,O, H,CrO H,SbO, (?H,Cr(SCy),) HVO. H2MoO4 (?H,V,O,) H,V,O, H,Ta,O, H,WO, $(?H M O_7, M = Mo, W, U)$ $(?H_2M_3O_{10}, M = Mo, W, U)$ (?H,Nb,O,s) HAuCy, (?H₂ZnO₂) (°HMnO,) HAuCl, HHgCl, H₂MnCl₆ HHgBr, HAuBr. H,MnCy. H,PtCl H FeCv. HHgI. H_sFeCy₆ H2PtCl H,HgCl, H.PtI. H.Pt(NO.). H.Pt(NO.).Cl. H.FeCy, NO H2HgBr4 H,CoCy_e H,CoCy_e H,HgI, (?HZnCl,) H.Pt(SCy). (?H,AlO,) (?HZn,Cl,) H.PtOy,

The isolation of some of the acids in the fore-

going list is doubtfut, these acids are placed in brackets. The compounds H_{*}AlO_{*} and H_{*}ZnO_{*} are also bracketed, because the reactions of these bodies show that they may be classed as feeble acids and at the same time as basic hydroxides

An examination of the composition of the metallic acids shows that the reacting atomic aggregates of these compounds all contain a number of atoms of a negative element, or group of elements, which is large relatively to the number of atoms of metal present The accumulation of negative atoms so modifies the functions of the H atoms that these are replaceable by metals, and this notwithstanding the presence of the positive metallic atoms. The H of the of the positive metallic atoms metallic hydrogen - containing compounds $H_2Cr_2O_4(=Cr_2O_3H_2O)$ and $H_2CrO_2(=CrOH_2O)$ is not replaced by metals when these compounds react with metallic hydroxides or carbonates, but when 4 atoms of the negative O are associated with one atom of Cr and 2 atoms of H, the H of this compound (H,CrO4) is distinctly acidic The negative character, or acid forming character, of the groups CN and SCN is rendered evident by the number of acids which are formed by the union of these groups with H and metals

If attention is paid to the general chemical characters of the inetals which form acids it is seen that most of these metals occur in groups (using this term as it is used in the nomenclature of the periodic law) which also contain several distinctly non metallic elements—thus Ti, Sn, and Pb belong to Group IV, which group contains C and Si, Cr, Mo, W, and U belong to Group VI, in which group also occur the negative elements O, S, Se, and Te, As, Sb, V, Nb, and Ta form part of Group V, which is distinctly negative in its general chemical character, and includes the markedly non metallic elements N and P, I'e, Co, Ni, Au, and the Pt metals occupy a peculiar position in Group VIII (cf. Classification, vol in pp 203-210, also Iron Elements, this vol p 65)

Several salts exist which, on account of their methods of formation and general stability, are probably best regarded as derivatives of metallic acids that have not yet been isolated, among such salts may be mentioned the stanno- and zircono fluorides Mr₂Sn(Zr)F₂. Some chemists would class most, if not all, the double metallic haloid compounds as salts of metallic acids, e g BiF, 3KF as the K salt of the acid H₂BiF₆, ZnCl₂BaCl₂ as the Ba salt of the acid H₂ZnCl₄, and MgI₂KI as the K salt of the acid HMgI₃ (v. especially Remsen, Am 11, No 5)

The consideration of those metal-containing compounds which are acids brings out the in adequacy of that classification which would divide the elements into two classes only, metals and non-metals, it also well illustrates the difficulties of chemical classification, as shown by the way in which the chemical properties of an element are modified according to both the nature and the number of other elementary atems with which that element is combined (cf the article Metals in this yol and Classification in yol ii)

METALLOIDS This name was at one time applied, most mistakenly, to the non-metallic elements. It is sometimes used to denote those slements which on the whole are non-metallic,

but yet closely approach the metals in some of their properties, As, Sb, Ti, V, Nb, Ta, for instance, are sometimes called metalloids. The term cannot be defined. There are certain elements which one chemist would class among metals, another would place with the non metals, and a third would prefer to put into neither class, but call them metalloids

M M P M
METALLURGICAL CHEMISTRY The
chemical reactions utilised in metallurgy are divisible into two distinct classes, viz 'wet,' those
which take place in aqueous solutions, and 'dry,'
those which take place in furnaces, or their
equivalent, at a relatively high temperature
The present tendency is more and more in the
direction of combining these two methods, metals
being now frequently extracted from their ores
partly by wet processes and partly by dry processes

The ore of any metal may be defined as a collection of mineral substances containing that particular metal in sufficient quantity to pay for its extraction on a commercial scale. Although each metallic element exists in nature in a great number of combinations, yet very few of these compounds occur in sufficient quantity to be of direct importance to the metallurgist, except in so far as they may tend to introduce impurities into the metal to be extracted.

Chemically, ores may be broadly divided into three classes, containing respectively—I NATIVE METALS, i.e. metals uncombined with any non metallic element II SULPHIDES and ARSENIDES III Oxides, including carbonates and silicates

Class I NATIVE METALS A native metal may be separated from its ores in one of four ways (a) By Liquation In order that this may be done it is essential that the metal be fusible at a temperature insufficient to cause the earthy portions of the ore to frit or agglomerate, eg B: (b) By fusing the ore, when the metal will sink to the bottom by reason of its high SG, eg Bi, Cu (c) By dissolving the metal out by means of another metal, eg Au, Ag, Pt These metals may be dissolved out of their ores by Pb, which is then removed by cupellation, or, in the case of Ag, the separation of the Ag from the Pb may be effected by Zn, which does not alloy with Pb, and being specifically lighter rises to the surface, The Zn carrying the Ag and some lead with it is subsequently distilled off, and the residual Ag and Pb cupelled Similarly, Au and Ag may be dissolved out by Hg, which may then be distilled off (d) By dissolving the metal by means of an acid or a gas in solution, eg Au extracted by a solution of Cl, and Pt, Pd, Ir, Rh, and Ru by aqua regia The Au and Pt may be refined by wet processes, taking advantage of the fact that Au and Pt are insoluble in sulphuric. hydrochloric, and nitric acid, when these acids are used separately, but are soluble in aqua regia, while the Ag, Cu, Pb, and Fe are freely soluble in one or other of the three acids named In 'parting' Au, sufficient Ag must be present to allow the acid free access to the impurities, which would otherwise be protected by the insoluble gold Pt, when present in Au only in small quantity, may be separated by 'parting' with Ag, as under these conditions the Pt is

soted on by the 'parting acid' If present in larger quantity, it must be ppd from a solution. Ir may be separated from Au by difference of SG, and from Pt it may be removed to a certain extent by using aqua regia of medium concentration, in which it is not freely soluble Pt is ppd from its solutions as a double salt of Pt and NH, by adding NH,Cl Pd, if present, may be ppd before the Pt by neutralising with Na,CO,Aq and adding HgCy, Ir, if it has gone into solution, will not be ppd with the Pt, but its double salt is difficult to wash out Pd. Rh. Ru, and Os will also be found with the Ir in solution after the Pt has been ppd Rh may be removed completely by fusing the platinum double chloride with KHSO, and a small quantity of NH HSO. Ir may be ppd at the same time as platinum by KCl, and the pp fused with K CO, which will oxidise the Ir and not the Pt Remove the potassium salt by boiling water, and then dissolve out the platinum with aqua regia, in which the oxide of Ir is insoluble Ir may also be separated from the pp by KCy, the Ir salt being soluble while the Pt salt is insoluble Pt is obtained in the metallic state by carefully heating the double chloride, which then breaks Au is ppd from its solutions as metal by FeSO, Aq, SO, Aq, or H2C, O, Aq For dental purposes, Au is frequently deposited by electrical means Ag is first thrown down as chloride, which is afterwards reduced by Cu, Zn, or Fe Au, containing not more than 10 p c Ag, is also refined by Miller's process, at the Australian Mint, in the dry way, by passing Cl into the molten gold The impurities As, Sb, Bi, Pb, and Zn are converted into chlorides, which volatilise, and the Ag becomes AgCl, which forms a fused layer on the surface of the gold

Class II Sulphides and Arsenides Dry methods Sulphides and arsenides are either (a) infusible, at such temperatures as can be obtained in furnaces on the large scale, (b) fusible,

or (c) volatile without fusion

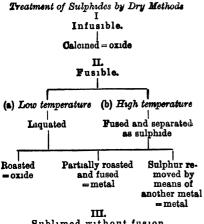
(a) Infusible sulphides In these cases the S must be replaced by O, as an infusible sulphide cannot be properly reduced to the metallic state. This is done by calcining or reasting the ore, so that air has free access to it. The sulphide is exided to a sulphide at low temperatures, and at higher temperatures the sulphide breaks up into SO₂ and an exide of the metal. Practically there is only one sulphide under this head, viz ZnS, sinc blende. For the subsequent treatment of the exide v 'exide class'

(b) Fusible sulphides Sulphides and arsenides of this class may be subdivided as follows—(i) those which are fusible at a very low temperature, insufficient to produce fritting, is incipient fusion causing agglomeration of the constituents of the ore, (ii) those requiring a higher temperature, at which fritting would take place A sulphide in division (i) may be liquated out, e.g. Sb₂S₂. The sulphides and arsenides belonging to (ii) may be separated by fusing the ore, when the sulphide or arsenide would collect together beneath the slag, e.g. sulphide of copper (copper pyrites), arsenides of nickel and cobalt (if sufficient arsenic is not present in the ore more is added), the arsenide separates in a distinct layer from the sulphides of other metals during the

fusion, sulphide of nickel obtained by fusing nickel ores, or products, free from arsenic, with iron pyrites The sulphides and arsenides thus separated from the gangue would next be treated in one of the following ways —1 Converted into oxide by roasting, e.g. Sb.S., copper matte, arsenides of nickel and cobalt (the arsenious and being condensed in coke towers), sulphides of nickel and cobalt free from arsenic, the oxides of nickel and cobalt are subsequently treated in the wetway 2 Partially roasted to form a certain amount of oxide and sulphate, and then fused, the oxygen of the oxides combines with the sulphur of the sulphides and arsenides, forming SO, and liberating the metal, eg Sb₂S, and PbS In the case of the double sulphide of Cu In the case of the double sulphide of Cu and Fe, the Fe is first removed by a series of calcinations and fusions, S passing to the Cu and O to the Fe, the oxide of iron thus formed uniting at the same tune with silica to form slag This process goes on so long as any iron As soon as the iron is all removed, remains the reaction between Cu₂S, CuO, and Cu₂O takes place, liberating metallic copper principal impurities in copper ores likely to pass into the Cu are As, Sb, Zn, Pb, Bi, Sn, Ni, Co, Au, and Ag The greater proportion of these present either volatilises or becomes oxidised and removed in the slags Au and Ag, being neither appreciably volatile under the conditions nor oxidisable, become concentrated in the copper It is particularly difficult to get rid of the last The use of a basic lining traces of As and Bı to the furnace—say, dolomite—greatly facilitates the removal of As in the slag The elimination the removal of As in the slag of As is also assisted by the use of 'soda nitre' in refining Bi can most readily be removed by what is known as the best selecting process, in which advantage is taken of the circumstance that copper has a greater affinity than bismuth for sulphur This process comes in just before the copper is first reduced from the sulphide little copper is made to separate by the reaction between sulphide and oxide, this throws out and collects as 'bottoms' the bismuth, tin, lead, and antimony -3 Fused in the presence of another metal which combines with, and so removes, the sulphur, eg sulphides of Bi, Pb, and Sb treated with Fe, Ag separated by metallic Pb from sulphide of Ph containing sulphide of Ag Copper can only be partially separated from sulphur in this way, a double sulphide forming which cannot be reduced by iron

The operations described under (1) and (11) are in some cases applied directly to the ore without first separating the sulphide by liquation or

(c) Sulphides volatile without fusion Amongst the metallic sulphides there is only one which sublimes without fusion, viz HgS When heated in presence of air HgS yields SO₂ and Hg As the Hg has no tendency to combine with oxygen under these conditions, and is vilatile at a very low temperature, it distils ever, and may readily be condensed For these reasons advantage is not taken of the fact that the sulphide is itself volatile, it being simpler to distil the metallic mercury direct from the ore The sulphur is sometimes removed by roasting the mercury ore with lime or oxide of iron.



Sublimed without fusion 1 Sulphur separated by calcination alone = metal

2 Sulphur separated by lime, oxide of iron, or iron = metal

Wet processes for sulphides and arsenides The sulphide and arsenide ores of Ni, Cu, and Co are partially, and those of Cu and Ag partially or wholly, treated by wet methods In these processes the metal is first made to form a soluble compound This may be done by roasting the ore with, or in some cases only mixing it with, some compound, which by double decomposition will convert the metal to be extracted into a soluble compound In other cases it is done by roasting the ore alone at a low temperature, or even by simply exposing it to the action of the atmosphere without using artificially produced heat, in either case the sulphide will be con verted into a sulphate, eg copper pyrites and silver ores

Thus, soluble sulphate of copper may be formed by roasting copper pyrites or more slowly at the ordinary temperature of the atmosphere About one third of the copper extracted in this country is obtained from Spanish pyrites, averaging only 3-4 pc of copper, by roasting the burnt ore received from the sulphuric acid works-with common salt, which reacts with the CuSO, produced during the burning, to form CuCl2, which is then dissolved out, together with the chlorides of Ag, Pb, and Au, these metals being present to a small extent The Ag is thrown down, along with Au and Pb, by a soluble iodide, KI or ZnI2 The iodine is removed from the AgI by Zn Finally the Cu is ppd by addition of iron

The reactions which take place in the wet treatment of silver ores are of special interest They are divisible into three and importance classes

I The insoluble silver compound is decomposed and the Ag amalgamated while still in the ere ('free milling ore'), without the aid of any furnace-operation whatever If there is much S or As present the ore, where practicable, is first roasted with salt Under this head are included all the amalgamation-processes

II. The mealuble silver compound is converted

unto sulphate by roasting alone and washed out with water, or the Ag is converted into chloride by roasting with common salt, and washed out by a solvent for chloride of silver Under this head are included the Augustin, Ziervogel, Von Patera, and Russell processes

III The insoluble silver compound is converted into a soluble compound by the action of certain salts in solution without roasting the ore or employing any furnace-operation whatever This class includes the Von Patera process when applied to 'amalgamation tailings,' and the Russell process applied to both ores and tailings

The amalgamation methods without roasting have been of great service where fuel is scarce, as in Mexico These methods depend on the power of Gortain salts, such as the chlorides of Cu, to decompose Ag₂S If mercury is present at the same time, the AgCl will be reduced and the Ag taken up by the excess of Hg, from which it can be separated by squeezing and distillation Iron or Cu may be employed to decompose the AgCl, Hg being used only to collect the Ag This reduces the loss of Hg, but to bring about suffi cient contact, more power, and consequently more fuel, is required Where fuel is available there is often great advantage in roasting the ore with salt before amalgamation

Where possible the amalgamation methods have been superseded by the other wet processes included under heads II and III, viz the Augustin, Ziervogel, Von Patera, and Russell methods

The Augustin process Ore or regulus is first partially roasted, and then undergoes further roasting with common salt, the AgCl thus formed being washed out with NaClAq and ppd The Ag is usually first concentrated in by Cu copper mattes

The Ziervogel process This method depends on the difference between the temperatures re quired to break up the sulphates of different Thus by suitably regulating the tempe metals rature, the sulphates of Fe, Cu, &c, formed by roasting mattes at a low temperature, may be de composed into oxides and SO2, while the sulphate of Ag will be unaltered, and can therefore be ex tracted by warm water, and then ppd as in the previous method The regulation of the tempe rature throughout a large furnace is obviously a point requiring considerable skill reason, in practice, matter are usually first worked by the Ziervogel process, and the residue ex tracted by the Augustin method

Von Patera process The soluble salts pro duced by roasting the matte are first dissolved out with water, after which the matte is further roasted with NaCl, and the AgCl washed out with Na₂S₂O₃Aq or CaS₂O₃Aq, from which solu tion the Ag is ppd by a soluble sulphide or The silver is reduced from the Ag₂S, either SH, by roasting or by boiling with freshly slaked lime, forming calcium polysulphide When there is much of the base metals present, more particularly lead, the Von Patera process is not so suitable The lead is mostly present as sulphate after roasting, and this is soluble in Na₂S₂O₂Aq Some of the most important objections to the Von Patera process, as applied to poor ores containing base metal, are obviated in the process mext described.

The Russell process In this process what is known as the 'extra solution' is used, in addition to or in substitution for that ordinarily employed in the Von Patera process The 'extra solution' is prepared by making solutions of Na₂S₂O, and CuSO, containing respectively 18 parts of the former and 10 parts of the latter salt, and mixing them together The pp after washing is dissolved in a solution containing 1-21 p.c Na₂S₂O₃ Although this 'extra solution' is not so good a solvent for AgCl as Na,S,O,Aq, yet it acts energetically on native silver and the compounds of silver with S, As, and Sb Owing to the want of permanence special precautions have to be taken in using this solution. To get the best effect the solutions should be used warm In order to obtain finer bullion by this process, ad vantage is taken of the fact that PbCO, is not soluble in the solution, although other salts of lead are soluble Na₂CO₃, free from NaOH and Na2S, is added to the solution containing the silver and lead which have been washed out It is stated that the whole of the Pb may thus be Carbonate and sulphate of Cu are the only compounds of Cu likely to occur which are soluble in the 'extra solution'

It is probable that this process in the near future will supersede very largely the fusion and amalgamation piocesses, besides which it is applicable to cres which cannot profitably be treated by either of the other methods. The cost of the necessary chemicals is much less than that due to loss of mercury, in addition to which, lead and copper are lost in the older processes and saved in the Russell process.

In some cases the ores may be treated direct by the Russell process without previous reasting, and both the Von Patera and Russell methods are largely used in the treatment of 'tailings' from amalgamation

Nuckel and cobalt It has been seen that these metals may be separated from others as arsenide In practice, however, the separation is not so complete, some of the nickel and cobalt passing into the regulus, and some of the other metals into the spesse. The following are the reactions usually employed to separate the va rious metals from one another The calcined speise is treated with HClAq The resulting so lution, which will contain Ni, Co, Fe, Cu, Pb, Bi, and As, is diluted, and oxidised by bleachingpowder, the proportion added being adjusted by a rough analysis Milk of lime is added to the requisite extent to throw the iron down as ses quioxide, any arsenic present at the same time ppg as basic arsenate of iron The solution is next treated with SH, to ppt Cu, Pb, and Bi, after which the Co can be thrown down as ses quioxide by a further addition of bleachingpowder, and subsequently the Ni ppd as hydrated oxide by the addition of milk of lime

Class III Oxides, including carbonates and bilicates Ores of this class are reduced to the metalic state by means of carbonaceous matter such as charcoal, coal, or co'e, or by means of the gaseous product of the incomplete oxidation of carbonaceous matter, vis carbon monoxide

The only exceptions among the oxides of the commoner metals are Al₂O₂ and MgO These oxides cannot be reduced to the metallic state in this way; they have to be converted into

double chlorides, from which, while in a state of fusion, the metals are liberated by metallic The metals, the sodium, or by electrolysis oxides of which are in practice reduced by car bon or CO, are Sn, Fe, Ni, Co, Mn, Cr, W, and Zn Of these Sn and Zn present the simplest The reactions in the other cases are complicated by the fact that all these metals combine more or less freely with carbon When it is desired to obtain the metals in the most malleable condition, se free from carbon, the fact that the oxides and the carburised metals react with one another eliminating both the carbon and the oxygen, as CO and CO₂, is utilised Every iron- and steel making process is dependent on this reaction. According as the conditions are made more or less favourable to carburisation, or decarburisation, so will the resultant metal be either cast iron, hard steel, mild steel, or malleable iron. It is possible to reduce the oxides under consideration to the metallic state, and also to carburise the metals, by the action of CO, without the metals becom ing fused The oxides are first reduced, and then carburised by the dissociation of some of the CO The liberated oxygen combines with CO and is thus removed Nickel is thus reduced to the metallic state, more or less combined with car bon, and bars of metallic iron are carburised to produce 'cementation' steel In a similar way a carburised metal may be decarburised by O or CO2, in this way 'malleable cast iron' is made Whether the action consists of carburising or decarburising is entirely dependent on which agent preponderates at the time in the atmosphere surrounding the body

Reactions for removal of 'impurities' from metals of oxide class The refining of Ni and Co, as we have seen, precedes the reduction to the metallic state The refining of Sn is effected after reduction, partly by liquation and partly by oxidation, by which means the principal im purities, Fe, As, and W, are removed Mn and Cr are reduced directly from their ores, in the form of alloys with iron, only pure ores being used Tungsten is either reduced directly from the ore, alloyed with iron, or undergoes a preliminary purification and ppn as oxide in the wet way The impurities which it is important to remove from iron are S and P The latter can only be passed into the slag when the slag is basic, and the conditions tend to oxidation Thus, P is removed in the primitive iron making processes, also when iron is made by the 'finery' and the 'puddling' processes, also in making 'ingot-iron' by the Siemens and Bessemer processes, when a basic lining to the furnace or converter is used P is not removed in processes in which pig iron or high carbon steel is made, nor in the Siemens or the Bessemer processes when the furnace or converter is lined with siliceous material, and malleable metal is being produced In the Bessemer process, with an acid hning,' the necessary heat for the process is obtained mainly by the oxidation of silicon in the pig-iron, when a phosphoriferous pig iron is used, and a 'basic lining,' most of the heat is obtained by the oxidation of the phosphorus and less silicon is required in the pig-iron In both pro cesses a portion of the heat is obtained from the exidation of C Sulphur can be removed economically only in the blast furnace, because when treating pig-iron for the production of malleable iron the sulphur is one of the last substances to oxidise out, and its removal would result in a great waste of iron. To remove S in the blast-furnace the temperature must be high, and the conditions must be strongly reducing and carburising: *e the charge must contain plenty of charcoal, coal, or coke, and lime must be added to the charge in considerable quantity. Under these conditions the S combines with the Ca, and passes into the slag as sulphide

SLAG REACTIONS Slags consist of the normetallic constituents of an ore or furnace pro duct, and of the useless or objectionable metallic They are produced by simply fusing the ore alone, if it is in itself sufficiently fusible, or by fusing it with such materials-fluxes-as will bring about the requisite fusibility Except in a few special cases, eg the reduction of aluminium or magnesium, slags consist of more or less complex silicates In processes for making more or less malleable iron, the slags are com posed mainly of silicates of Fe, Ca, Al, and Mg, with smaller proportions of silicates of Mn, alkalis, and alkaline earths In pig iron slags, the iron is comparatively small in quantity, or is even entirely absent when much lime is used In other slags, excepting those produced in treating the 'noble metals,' iron will generally be

present in large proportion

ELECTRO METALLURGY Electro metallurgical processes are divisible into two distinct classes one class includes processes for the extraction of metals from their ores, the other includes processes for refining metals already extracted Although a great many processes have been devised for the electrical extraction of metals, except for the extraction of aluminium and magnesium-in which cases the metals are first got into the condition of double chlorides, or, in the case of aluminium, sometimes of fluoride -there is not much prospect of such processes being successfully and economically worked, even when power can be obtained from water-falls By the Cowles process, according to Sterry Hunt, nearly pure Al is produced in small buttons, but up to the present it has been necessary to reduce some other metal with the Al to collect it together In this process the Al₂O₃ and the oxide of the metal to be alloyed with the Al are mixed with carbon, and the mixture is placed round two carbon poles between which an electric discharge is made to pass

The second class of processes has been advantageously applied to the refining of Cu, more particularly Cu containing small quantities of Au and Ag In refining Cu electrically, the electrolyte is usually CuSO₄Aq, kept at as uniform a temperature and concentration as possible, the anode being formed of the copper to be refined, pure copperdepositing on the cathode. The silver and gold collect at the bottom of the tank as a smiddy deposit.

muddy deposit.

METALS. An element is a definite and distinct kind of matter which has resisted all attempts to separate it into unlike portions. The classification of the elements, in accordance with their chemical properties, necessarily carries with it the classification of many compounds, insamuch as the chemical properties of an elements.

ment cannot even be stated without considering the composition, general chemical behaviour, and conditions of formation, of compounds of that element. For instance, certain elements are placed in the same class because they all form hydroxides which are alkalis this state ment implies an acquaintance with the composition, methods of production, and chemical properties, of the alkalis, but one of the chemical properties of an alkali is that it neutralises acids, and in so doing forms salts, hence it is necessary to know something about acids and salts, in order to understand what is meant by an alkali, or by an alkali forming element.

The elements may be classified in accordance with their physical properties If a binary compound is electrolysed, one of its elements separates at the positive electrode, and the other at the negative electrode (secondary reactions which may occur are supposed to be overlooked) That element which separates at the positive electrode is said to be electro negative to the other element By studying the electrolysis of binary compounds, the elements may be arranged This series may be in an electrical series divided into two parts all the elements on one side of any chosen element are electro positive to all the elements on the other side of the chosen element Taking hydrogen as the central element we are able to subdivide the elements into two classes, all the elements on one side of H are electro positive to the elements on the other side of H Thus we arrive at a classi fication of the elements founded on one chemicophysical property Now we find that the electropositive elements, on the whole, more resemble one another in certain physical properties, and also in their general chemical character, than they resemble the electro negative elements Those elements which are electro positive to H as a class are greyish white in colour, lustrous, fairly malleable and ductile, comparatively good conductors of heat and electricity, those ele ments which are electro negative to H vary much in colour and appearance, they are not usually lustrous, they are generally brittle, and they do not conduct heat or electricity well to the chemical characters of the two classes of elements, we find that those placed in the elec tro-positive class generally combine with O to form basic oxides their compounds with O and H are also usually basic, they do not, as a rule, enter into the composition of acids, very few of them form hydrides, their haloid compounds, as a whole, are tolerably stable as regards the action of heat, and they are not readily decom posed by water, if they are thus decomposed they generally produce oxyhaloid compounds, speaking broadly, these elements do not exist in allotropic forms. On the other hand, we find that most of the elements which are placed in the electro negative class combine with O to form acidic oxides, their compounds with H and O are usually acids All acids contain one or more of these elements, they generally form hydrides, many of their haloid compounds are decomposed by heat, and many of them are also decomposed by reacting with water, thereby producing haloid acids and either oxides or oxyacids of the electro negative elements; speakMETALS. 241

ing broadly, these elements exhibit the phenomena of allotropy

Hence, it would appear that the division of elements into two classes, those which are electro positive to H, and those which are elec tro negative to H, is a good classification, because with this one class mark many other properties, both physical and chemical, are associated

The electro positive elements are called metals, the electro negative elements are called non metals

A further examination of metals and nonmetals shows that the classification implied in these terms is very far from being sufficient for chemical purposes We cannot define the term metal, just as we cannot define any of the chemical names which are given to classes of bodies We can sketch the ideal metal Considered physically, the ideal metal is a hard, fairly heavy, greyish-white, lustrous, malleable, ductile, and tenacious solid, which melts only at a high temperature, it is a good conductor of heat and electricity, it crystallises in forms be longing to the regular system, its emission spectrum consists of lines, and is comparatively simple in character Considered chemically, the ideal metal is hardly, if at all, changed in the air, it combines with O at fairly high tem peratures, and forms one or more oxides which are basic, te which react with acids to form salts, it reacts with water or steam to produce an oxide or hydroxide and evolve H, no hydride of the ideal metal is known, it does not enter into the composition of acids, but it reacts with acids to form salts, its sulphides react with acids to produce salts and evolve H2S, they combine with the sulphides of decidedly electronegative elements, the salts of the ideal metal are numerous and stable, it forms but few acid salts, but the number of double salts into which it enters is large, it combines directly with the halogens, producing compounds which are vola tilised without decomposition at rather high temperatures, and which dissolve in water without change, the ideal metal forms alloys with elements of its own class, which alloys be long rather to the group of physical, than to that of chemical, compounds, lastly, the ideal metal exists in only one modification, se it does not show allotropy The ideal non-metal is the opposite, chemically and physically, of the metal

No element exhibits all the properties which we have placed in the category 'metal', nor is there any element which possesses even some of these properties without at the same time also possessing some of the properties which belong to the typical non metal

The elements sodium and potassium possess most of the chemical properties enumerated as characteristic of metals, but these elements are instantly oxidised by exposure to air, they pro-bably form unstable hydrides, they are very soft, lighter than water, and melt at moderately low temperatures.

The element gold possesses most of the physi cal properties characteristic of metals, but its hydroxide reacts with alkalis to form salts, eg KAuO,; Au also forms the acids HAuBr, and exhibits any acidic functions, they are electro-HAuOl4; Au₂S combines with the sulphides of positive to all the other elements. The metals Vor. III.

the very metallic elements K and Na to form The element chromium exhibits many of the characteristic physical properties of metals, it also decomposes steam with evolution of H, it combines with the halogens to form stable compounds, some of which have been gasified at high temperatures, chromium does not form a hydride, the oxides CrO and Cr.O. are basic, the element reacts with many acids to form salts, which are well marked, stable compounds, it does not exist in allotropic forms. On the other hand, CrO, is a distinctly acidio oxide, reacting with water to form the acid H₂CrO₄, from which is obtained a large number of salts In other words, chromium belongs to the class metals, and also to the class nonmetals In an even more marked way than Cr, manganese combines in itself both metallic and non metallic properties

The chemical properties of an element depend on the properties of the other elements with which it combines, and on the relative quantities of these other elements entering into combination It is this fact which makes it impossible to apply the definition of metal or non metal, in its entirety, to any element The classification of elements into metals and non metals is nevertheless a useful one, provided it is employed with judgment and knowledge If we find that a certain element is hard, lustrous, unchanged or only slowly changed in the air, and is a good conductor of electricity, or if we find that the oxide of a certain element is basic, and that the chloride is not decomposed by water, or if decomposed produces an oxychloride, we have at once a guide to lead us in our further examina-tion of the element. We shall probably find that the element in question possesses several of the other physical characteristics of metals, and we shall also probably find that it reacts with acids to form salts, decomposes steam with evolution of H, produces at least one sulphide which combines with sulphides of some of the negative or non metallic elements, and so on

The following division of the elements usually placed in the class metals is that arising from the application of the periodic law

```
CLASS I division 1, Li Na K Rb Ca
  CLASS II davision 1, Be Ca Sr Ba
                    2, Mg Zn Cd Hg
 CLASS III division 1, Se Yt La Yb
 ,, 2, Al Ga In Tl.
CLASS IV division 1, Ti Zr Ce Th
  ", 2, Ge Sn Pb
Class V division 1, V Nb Di Ta
 CLASS VI dursion 1, Cr Mo W U
                    2, none isolated.
 CLASS VII division 1, Mn
                    2, none isolated.
CLASS VIII division 1, Fe Ni Co (Cu)
                    8, Os Ir Pt (Au)
```

The metals in division 1 of Class L are generally known as the alkalı metals They possess in the most marked way the chemical characters of the ideal metal; none of their compounds exhibits any acidic functions, they are electro-

R

METALS. 249

in division 2 of Class I are very distinctly metallic in their physical properties, chemically considered they show considerable differences among themselves, several compounds of gold are almost non metallic in their reactions, the chemical and physical analogies of this element are best represented by placing it both with Cu and Ag, and also with Os, Ir, and Pt, in division 8 of Class VIII

The alkaline earth metals which form divi sion 1 of Class II are more metallic in their physical properties than the metals placed in division 1 of Class I , chemically they are also distinctly metallic Coming to Mg, Zn, Cd, and Hg, which form division 2 of Class II, we have four elements whose properties closely approach those of the ideal metal, Cd may be taken as on the whole the best actual representative of the class metal As we pass to the higher classes we find many metals exhibiting properties characteristic of non metals, until in Class VII we arrive at Mn, an element which is at once distinctly metallic and decidedly non-metallic in its chemical properties

In connexion with the subject of this article, reference should be made to the following articles wherein the different classes of metals are described - Alkaline earths, metals of the, vol 1 p 112, Alkalis, metals of the, vol 1 p 114, CHROMIUM GROUP OF ELEMFNIE, vol 11 p 168, COPPER GROUP, Vol 11 p 250, LARTHS, METALS OF THE, Vol 11 p 424, IRON GROUP, Vol III p 65, MAGNESIUM GROUP, vol III p 163, NITROGEN GROUP (for Class V, V to Bi), vol III infra, Noble metals, vol 111 infra, Titanium

GROUP, in vol iv , Tin GROUP, in vol iv

M M P M METALS, RARE Under this name are in cluded a number of presumed elementary bodies concerning which our knowledge is at present very imperfect. We see that in their general properties they approximate more or less closely to cerium, yttrium, and lanthanum, but we are not sure how far we have yet obtained them in a state of purity Consequently we are in doubt not merely as to their at w and SG, but even as to their number and their rank as elements, compounds, or mere mixtures Our ignorance is due to the great rarity of these bodies, to the high complexity of the minerals in which they are found, but most of all to the fact that they differ among themselves merely by very minute shades

The principal sources of the rare metals are gadolinite, keilhauite, fergusonite, euxenite, cerite, and thorite, which are Norwegian minerals, and further, samarskite, which was first obtained from the Urals, but has since been found in relatively large quantities in North Carolina It is to be noticed that specimens of any one of these minerals, if from different localities, are not identical in the earths they contain Hence if it is desired to isolate any particular earth it is best to select as the first material that mineral in which nature has, so to speak, commenced the task of separation (This method was proposed by the writer in his address to the chemi-cal section of the British Association, Birmingham Meeting (C N 54, 128, abid 54, 157, Pr 40, 505) Nilson a Krüss have since adopted and recommended the same method (B 20,

2134, C N 56, 74, 85, 135, 145, 154, 165,

The recognition of the various rare earths is a matter of no little delicacy Here spectroscopy in its several modifications renders the greatest service In endeavouring to ascertain by this means what substances are present in a mineral containing rare earths, chemists may employ either the spark spectrum, the absorption spec trum, or the incandescence or the phosphores cence spectrum They may further apply any of these tests either at once to the original matter, or to some of its portions after a partial separation has been effected by chemical treatment question of course arises, how are we to know when we have obtained any one earth separated from all other bodies, and absolutely pure? In the case of those earths and their solutions which present an absorption spectrum, e g didymia, samarıa, holmıa, erbıa, &c , the writer has shown that as an element approaches simplicity the absorption spectrum of its solutions will become less and less complicated, hence it would appear that when absolutely free from its associates, each element would have an absorption spectrum of great simplicity, in many cases consisting of one band only (the 'one band, one element' hypothesis) But as certain earths, e g lanthana, mosandra, philippia, scandia, terbia, &c , give no absorption spectra, this test is not applicable in all cases

Great caution is required in drawing conclusions from the examination of spectra. Concerning the influence of one body upon another little is yet known, but that little is of sufficient importance to make us very careful how we in terpret absorption-spectra when not corroborated by chemical results Lecoq de Boisbaudran a J Lawrence Smith have pointed out some im portant modifications produced in absorption spectra by the presence of an excess of acid in the solution (C R 88, 1167) Soret subsequently verified these observations Brauner and others have put on record experiments on mixing solu They find tions of didymium and samarium in the case of a didymium solution showing the group of three bands, 476, 469, 428 $[1/\lambda^2]$ 430 4, 441 3, 454 6], that, by adding a dilute solution of samarium, these three bands vanish, without the appearance of any of the samarium bands, until a certain proportion is reached, when the samarium bands gradually come into their places (Brauner, C J 48, 286)

Many of the earths that do not yield solutions giving absorption spectra can be made to give characteristic spectra by phosphorescence This is known as the 'radiant matter' test When the spark from a good induction coil traverses a tube having a flat aluminium pole at each end, the appearance of the spark changes according to the degree of exhaustion If atmospheric air is the gas under exhaustion, at a pressure of about 7 mm a narrow black space is seen to separate the luminous glow and the aluminium plate connected with the negative pole of the induction coil As the exhaustion proceeds this dark space increases, until at a pressure of about 002 mm the dark space nearly fills the tube; the luminous cloud showing the presence of residual gas has almost disappeared, and the molecular discharge from the negative pole begins to excite phosphorescence on the glass where it strikes the side There is a very wide difference in the degree of exhaustion at which various substances begin to phosphoresce Under the influence of this discharge of ' radiant matter,' a great many substances emit, more or less intensely, a phosphorescent light examining this light in the spectroscope, most of these bodies give a faint, continuous, spectrum with a more or less decided concentration in some one part, the superficial colour of the phosphorescing substance depending on this preponderating emission in one or other part of the spectrum Sometimes, but less commonly, the spectrum of the phosphorescent light is discontinuous

If we examine the rare earths by this 'radiant matter' test we find they present phenomena of a striking character Some of them remain unaffected, and are thus at once referred to a distinct group Others, such as thoria, do not phosphoresce and offer great ob struction to the passage of the spark Other earths become very phosphorescent and vary greatly in their power of retaining a residual phosphorescence On examining phosphor escent earths glowing in a vacuum tube, the writer found remarkable differences in the dura tion of this residual glow. Some of the earths remain luminous for many minutes after the cessation of the current, while others cease to phosphoresce immediately on the stoppage of the current Take the case of yttria This Take the case of yttria earth, the writer finds, can be resolved by chemical treatment into a series of simpler bodies of unequal basicity, to which he has given the provisional designations of $G\alpha$, $G\beta$, $G\delta$, $G\zeta$, $G\eta$, and $S\gamma$ The after glow of these bodies differs somewhat in colour from that which the earth exhibits while the current is still passing The spectrum of the after glow also shows that some of the lines are missing In the electrical phosphoroscope—an instrument similar to Bec querel's phosphoroscope, but having the substance acted on electrically instead of by direct lightthe different bands of the new constituents of yttria (v infra) do not all appear at the same speed of rotation At the lowest speed the double greenish blue band of GB is first seen, followed next by the dark-blue band of Ga As the velocity increases there follows the bright citron yellow band of Go, and as the utmost speed approaches the red band of G(is seen, but not without difficulty As another instance, if lanthanum sulphate, with traces of Sm as impurity, along with a little lime is examined in the phosphoroscope, the band of Ge is visible at the lowest speed, Go follows at an interval of 0035 second, and the Ga band immediately afterwards All the earths of the yttrum and samarium groups yield discontinuous spectra when submitted to the induction discharge in vacuo

A modification of phosphorescence spectroscopy is produced by the previous addition of other earths to the specially phosphorescent earths. Lime exerts a remarkable action. By itself, it phosphoresces with a continuous spectrum, while yttria phosphoresces with a discontinuous spectrum. But if these two bodies are mixed together, the phosphorescing energy of the lime does not extend over the whole spectrum.

but concentrates itself in strengthening the yttria These bands become broader, but at the same time less sharply defined, in proportion as the lime is increased in quantity. Lime also the lime is increased in quantity. Lime also brings out the phosphorescent bands of samaria It also suppresses the sharp line So, the most striking feature in the phosphorescent spectrum shown by pure samarium sulphate On the other hand an addition of 'old' yttria deadens the other lines of samaria, but brings out the line 88 more Lanthanum sulphate in the 'radiant matter' tube phosphoresces with a reddish colour If lime is added to lanthanum sulphate the phosphorescence changes its colour from red to yellow Lime also brings out the bands of yttrium and samarium if these are present as impurities sensitive is this test that it will show the presence of one part of yttria or samaria in more than a million parts of lime When Go, Ga, and GB are present in small proportions with lime the bands of Go and Ga become intensified. but a dark space appears instead of the green band of $G\beta$ Hence if only a small trace of $G\beta$ is present in lime the green band is not only obliterated, but the quenching action suppresses that part of the continuous lime spectrum which has the same refrangibility as the GB line, and thus gives a black space in the spectrum

There are many instances of the modifica tions induced in the normal spectrum of one earth by the admixture of others when treated as anhydrous sulphates One of the most striking instances is that of a mixture of samaria with yttria, since the presence of even 40 pc of yttria practically obliterates the spectrum of samarıa The most minute proportion of lime added to samarıa causes the sharp line at $1/\lambda^2$ 269 to vanish, while at the same time it much intensifies the other bands (Tr, pt ii 1885, C R, June 15, 1885) The action of lime upon yttria is of great use in detecting very minute traces of this earth when in admixture with elements which would otherwise prevent its phosphorescence

Alumna is also active in inducing new spectra when mixed with the rare earths. A moderate amount of fractionation has enabled the writer to penetrate beneath the veil of red phosphorescence observed in crude alumina and to see a complicated sharp line spectrum (O N, 56, 62, 72). The new body of which glimpses have been obtained is probably one of the unknown earths in decipia, since the new spectrum may be fairly reproduced by adding one of the fractionations of decipia to alumina. Hence, it will be seen that the performance of a long series of check and counter-check experiments often becomes necessary before the presence or the absence of any particular earth can be inferred

The quantitative separation of the rare metals is much more difficult than their mere recognition. These substances are not linked to one another, or to other elements with which they are associated, by any strong affinities, but they are nearly identical in their behaviour and properties. Hence we have so far been unable to find any reagent or any mode of treatment which at once quantitatively separates one of these substances from all the others. We are therefore obliged to have recourse to tedious processes of fractionation.

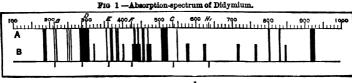
In attempting to enumerate or describe the rare metals, we meet with the additional difficulty that the unitary character of many of them is still a matter of extreme doubt

Several of the rare metals will be found described in their proper alphabetical order in this Dictionary, e.g. beryllium, cerium, didymium Many of these, as will be seen below, are probably capable of being further split up, but as they are frequently mentioned in chemical treatises and memoirs their description as at present, or lately, known has been found necessary

There are certain other metals which are still under discussion, eg decipium, philippium, holmium (Soret's X), and dysprosium Roscoe has indeed proved that philippium is a mixture of terbium and trinium, and the experiments of the writer have confirmed his results, but until we know more about the constitution of terbium and of yttrium, both of which are undoubtedly compound bodies, these experiments do not carry us much further Samarium is also identical

separate a mixture of two bodies into two parts, just as the addition of a reagent only divides a mixture into two portions, a precipitate and a solution These divisions will be effected on different lines according to the reagent employed Thus, if we add ammonia to a mixture we may get a separation into two parts, but if we add oxalic acid to the same original solution we split up the mixture differently and obtain two other parts Thus, if we erystallise a solution of old didymium, as was done by Auer von Welsbach, we divide its components into neodymium and praseodymium But by fusing didymium nitrate we divide its components in a different way and obtain different products Now, it is clear that so long as by different modes of attack we ob tain different products, we have not yet reduced the original substance to its ultimate elements, we have not yet reached bed rock

We find that a compound molecule may behave as an element, as has been shown in the case of old didymium Chemists have a certain



The scale is $\frac{1}{\lambda^2}$

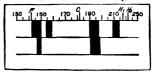
with a body which other chemists have named

It has been mentioned elsewhere that the old didymium, after the elimination of Delafontaine's decipium, was found by Lecoq de Boisbaudran to contain another body, which he named samarium, characterised by the bands of Delafontaine's decipium, together with two additional bands (cf figs 1 and 2) After the removal of these bodies the residual didymium was split up by Auer von Welsbach into the two bodies, neodymium and praseodymium, the absorption spectra of which are shown respectively in figs 3 and 4 It will be observed, however, that two of the bands of old didymium are not to be found in the neodymium and praseodymium spectra taken conjointly Hence it becomes extremely probable that there exists a third body distinct from neodymium and praseodymium to which one of these extra bands, or possibly both, This probable metal the writer has provisionally named Da But we still encounter the question whether neodymium, praseodymium, and Da are ultimate elements, or are capable of still further scission The researches of several investigators point very decidedly in the latter Thus Nilson a Kruss in 1887 appear direction to have obtained from didymium no fewer than nine bodies, each of which may possibly prove to be an element These bodies have been provisionally named by the discoverers $D_{1\alpha}$, $D_{1\beta}$, $D_{1\gamma}$, Dis, Die, Din, Die, Die, and Die

It seems to the writer that neodymium and praseodymium are simply the products into which the original didymium is split up by one particular mode of attack. Any single chemical operation, whether it be crystallisation, presipitation, fusion, partial solution, &c, can only

number of reagents, operations, or processes in regular use, and if a substance resusts all these and otherwise behaves as a simple body, they call it an element But for all this it may prove to be a compound Hence, we may legitimately pause before conceding to neodymium and praseo dymium the rank of elements We need some criterion for an element which shall appeal to our reason more clearly than the old untrust worthy characteristic of having not as yet been decomposed, and to this point chemists would do well to turn their most serious attention

Fig 2—Absorption spectrum of Samarium and Decipium (De Boisbaudran).



In samarium the writer, by means of the 'radiant matter' test, has recognised four bodies, named provisionally $S\delta$, $G\epsilon$, $G\gamma$, and $G\theta$ Very similar observations seem to prove that, like didymium and samarium, erbium, holmium, thulium, dysprosium, &c., are compounds or mixtures of a number of closely allied bodies

In order to ascertain the existence of supposed new elements chemists have proposed as a test that certain absorption-bands seen in different solutions follow the same variations of intensity. If this is the case we may infer that they are all characteristic of one and the same substance. But if one of the bands dies out while others remain unaltered we may judge that two or more distinct bodies are present.

In erbium the writer has detected two bodies, which he has characterised by their absorption bands \$550 and \$493 Kruss a Nilson apply apparently to the same bodies the names Era and Ers To obviate all confusion it must be remembered that the name 'erbia' has been given to two bodies which are not identical The substance which ten years ago was called erbia, and which was then supposed to be the oxide of a simple metal, has been resolved by the investigations of Delafontaine, Marignac, Soret, Nilson, Clève, Brauner, and others into at least six distinct earths. Three of these scandia, ytterbia, and terbia—give no absorption spectra, while three others - erbia (new), holmia, and thulia-give absorption spectra The first to question the elementary character of old erbium was Delafontaine (C R 87,559, C N38, 202) He obtained from it and described philippia, a yellow oxide having a strong band in the violet (\$\text{\$\lambda\$400 to \$405}), a broad black absorp tion band in the indigo blue (about \$\alpha450\), two rather fine bands in the green, and one in the red

The history of philippium is very instructive Soon after Delafontaine's discovery, Soret (C R 89, 521, C N 40, 221) stated that he was unable to identify 'Soret's X' with Delafontaine's philippia, the latter being characterised by an absorption band in the blue occupying the same place as one of the erbia bands In 1880 Delafontaine (C R 90, 221, C N 41, 72) described ten new earths as present in gadolinite and samarskite, viz, mosandra, philippia, ytterbia, decipia, scandia, holmia, thulia, samaria, and two others to which he did not assign names He concluded that the properties of philippia were identical with those of Soret's X and of Clève's holmia, and proposed that the name hol mia should be set aside in favour of philippia In C R 91, 328 (also C N 42, 185), Clève re peated his earlier assertion that philippia was not identical with Soret's X or holmia fontaine then withdrew all he had said about the absorption spectrum of philippium and decided that it had no absorption spectrum at all (Archives de Genève [3] 999, 15) Lastly Roscoe (C J 41, 277) gave an elaborate account of the earth metals in samarskite, proving philip pia to be a mixture of yttria and terbia present writer, after prolonged chemical exami nation of these earths, has come to a similar conclusion, but a spectroscopic examination of the earth left on igniting some very carefully purified crystals of philippium formate, tested in the radiant matter tube, has shown that in the separation of Delafontaine's 'philippium' the yttria undergoes a partial fractionation

Shortly after the announcement of philippium, Soret (C R 86, 1062) described an earth which he provisionally named X It was subsequently found to be identical with Clève's holmia (C R 89, 479, C N 40, 125) The absorption spectrum of this earth is marked by a very strong band in the extreme red (λ 804), two characteristic bands in the orange and green (λ 640 and 536), with fainter lines in the more refrangible part of the spectrum, and a number of bands in the ultra violet (see fig 7) The claim of holmium to rank as an element has been disputed by Nilson and Kruss, who assert that it consists of, or at least contains, four distinct

bodies, provisionally named $Xa, X\beta, X\gamma, X\delta$ By submitting Soret's X to fractional precipitation, and examining the fractions spectroscopically, Lecoq de Boisbaudran found that this X, otherwise holmium, consisted of at least two elements one of these he has named dysprosium, reserving the name holmium for the residue left after the elimination of the dysprosium. The absorption spectrum of dysprosium shows four bands, λ 4515, 475, 7565, and 4275. The absorption spectrum of what may be called new holmium is shown in fig. 8. What relation this new holmium bears to any of the components observed in the original spectrum of holmium by Krüss and Nilson is not as yet determined.

The writer (Pr~40,502) obtained an earth by repeated fractionation, in which one of the bands ascribed to dysprosium, that namely at $\lambda~451~5$, was very strong, though the others were absent As de Boisbandran regards the bands $\lambda~475$ and 451~5 as both belonging to dysprosium, and as the earth obtained gives $\lambda~451~5$ strong but with scarcely a trace of $\lambda~475$, dysprosium consists of at least two simpler bodies. Kruss and Nilson in fact resolve it into three bodies to which they have given the provisional names $X\zeta$, Xe, $X\eta$, and de Boisbaudran gives the absorption spectrum of

dysprosium as shown in fig 9

Simultaneously with the discovery of holmia, Clève announced the separation of a second earth from erbia, which he called thulia Its absorption spectrum consists of a very strong band in the red \(\lambda \) 680 to 707, and one in the blue \(\lambda \) 464 5 (fig 10) The ultimate character of thulium is by no means established Kruss and Nilson resolve it into two bodies, Tma and Tm3 Nevertheless the atomic weight of thulium has been determined as 170 7, and the composition Tm30, has been assigned to its oxide, determinations which for the present must be regarded as premature

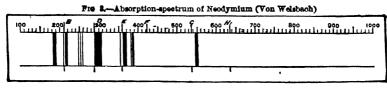
Further, it must be mentioned that the spec trum of old erbium has two faint bands, one at \$550 and a second broader one at \$493 (fig 11). These bands are not to be found in the spectrum of holmium, thulium, dysprosium, or the new erbium (fig 12). In a long continued fractionation of the erbia group of earths, conducted with an ample supply of the old erbia, the writer finds an earth giving these two bands concentrated at one end, the bands becoming stronger, while at the same time two other bands make their appearance. This phenomenon indicates the existence of another earth as yet unknown, belonging to the erbium group

We next come to the yttrium group, comprising the metals yttrium, terbium, gadolinium, ytterbium, scandium, mosandrium, columbium, and rogerium Of these yttrium, terbium, ytterbium, and scandium form the subject of distinct

articles in this Dictionary

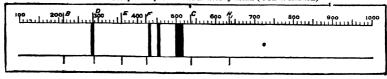
Columbium and rogerium were discovered in the samarskite of North Carolina by J Lawrence Smith in 1879, but nothing further has been published concerning them. This columbium is perfectly distinct from an element sometimes called columbium, but better known as tantalum.

Mosandrum was also discovered by J L. Smith, and has been the subject of a little controversy. Delafontaine pronounced it a mixture



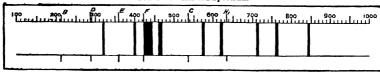
The scale is $\frac{1}{\lambda^2}$

Fig 4.—Absorption-spectrum of Praseodymium (Von Welsbach)



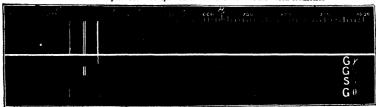
The scale is $\frac{1}{\lambda^n}$

Fig 5 -Samarium Spectrum



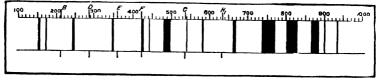
The scale is $\frac{1}{\lambda}$

Fig. 6 — Phosphorescence-spectra of Samarium and its Meta-elements



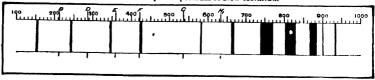
The scale is $\frac{1}{\lambda^n}$

Fig 7 - Absorption spectrum of Holmium.



The scale is $\frac{1}{\lambda}$

Fig 8 -Absorption spectrum of New Holmium



The scale is $\frac{1}{\lambda^2}$

METALS, RARE.

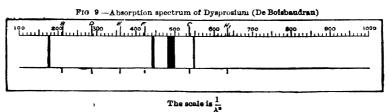
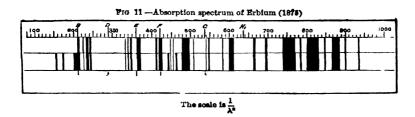
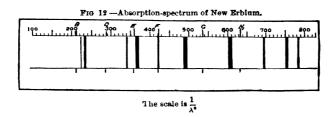


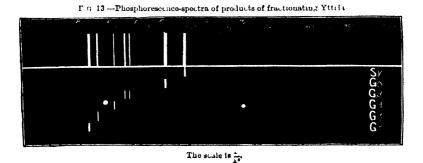
Fig 10 — Absorption spectrum of Thullum

190 299 500 500 500 1000

The scale is $\frac{1}{3}$







of terbium, yttrium, erbium, didymium, and philippium In November 1878 and in September 1879 Smith reasserted the elementary character of mosandrum He states that its compounds are of a deep orange colour, that its double potassium sulphate is not easily soluble, and that its equivalent weight is 512 No recent and conclusive investigations on this alleged metal have appeared, and its existence must in the meantime be regarded as exceedingly doubt ful

Decipium has been considered as holding an intermediate position between the didymium and the yttrium groups of rare metals, but its elementary character is very questionable. It has not formed the subject of any recent researches. It is said to show a characteristic absorption band about \$\lambda\$ 416

Gadolinium, otherwise known as the Ya of Marignao, gives no absorption-spectrum. In the writer's investigations its phosphorescence spectrum was found to consist of those of two of the constituents of yttrium, which will be mentioned

below

Yttrium proves to be an exceedingly complex substance The body to which all chemists would have applied the name yttria as recently as four years ago may be split up into possibly six, but certainly five, bodies, $G\alpha$, $G\beta$, $G\delta$, $G\zeta$, and $G\eta$, two of which, $G\beta$ and $G\zeta$, are also met with as the components of gadolinium Hence it is con venient to speak of the original substance as 'old yttria' and to remember that such is the substance to which everything written concerning yttra prior to 1885 will be found to refer Fig 13 shows the simple phosphorescence spectra of the several components into which yttria may be split up by fractionation If these com ponents are taken in the order of their apparent basicity—the chemical analogue of refrangibihty-the lowest of these constituents gives the deep-blue band Ga then follows a strong citron band, Go, which increases in sharpness as it becomes more separated from its associates un til it may be called a line, then a red band, G(, then a crimson band, $G\eta$, and, lastly, very close together a pair of greenish-blue bands, $G\mathcal{B}$

The diagram, fig 14, shows a series of nine teen phosphorescence spectra obtained from a prolonged examination of 'old yttria' The central spectrum, s, is approximately that given by crude old yttria, though this differs slightly according to the mineral from which the old yttria is extracted After a time fractionation splits up the earth J into two earths here marked I and K, giving slightly different spectra tionating I gives H and J, while K on fractionation yields J and L. It must not be thought that there is so great a difference between any two adjacent spectra as is here shown To make the diagram accurately represent what is actually seen in the laboratory it would be necessary to place between each of these nineteen spectra about 1,000 intermediate spectra. Beginning at the extreme red it will be seen that a strong band at $\lambda 647$ [1/ λ^2 289] is at its maximum intensity from 6 to E, when it rapidly disappears and is not seen beyond c and w. The component giving this band the writer names provisionally Gn The next band in the red $\lambda 689$ [1/ λ^2 245] reaches its maximum at A or even higher, and fades out be-

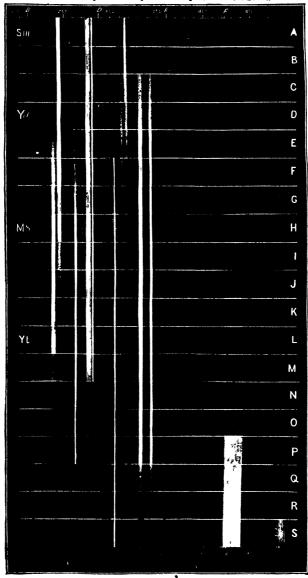
tween κ and κ . The band at $\lambda 619 \left[1/\lambda^2 261\right]$ has its maximum between I and o, dying out rapidly below but being more persistent above It is called G. Then comes an extremely sharp band $\lambda 609$ [1/ λ^2 269] which appears to belong to an earth absent in gadolinite but present in samarskite and a few other minerals greatest brilliancy is between E and K, and on either side it dies rapidly away. For this the writer proposes the name So. Then follows a double orange band, and its two components, though very closely united, are probably capable The maximum brightness of the of separation first component $\lambda 603$ [1/ λ^2 275] extends from o to the top of the figure The second component $\lambda 597 \left[\frac{1}{\lambda^2} 280 \right]$ begins to fade about q, and is at its greatest brilliancy at the highest spectrum shown on the figure. This band occurs almost isolated in a specimen of crude lanthana, and may be provisionally called Ge Next follows the citron, or G5 band, $\lambda 574$ [1/ λ^2 305 5] which is the most prominent feature in the spectrum of This band extends with scarcely old yttrium diminished sharpness from a to s, above a it fades rapidly and disappears above D follows a double green band separable into two components The first of these, $\lambda 568 \left[\frac{1}{\lambda^2} \right]$ is nearly absent in A, reaches a maximum at D, and disappears at κ The second member of this green pair, $\lambda 563 [1/\lambda^2 315]$ has its maximum at A and extends only to H The substance pro ducing this pair of bands may be called for the present Gy Then follows a pair of bright green bands which so far show no signs of dividing They begin at B, reach a maximum at E, and continue with scarcely diminished brightness to The body giving this double green band is remarkably persistent and may provisionally be called GB Next comes a dark interval followed by a broad, hazy, double blue band, with its centre at $\lambda 482 [1/\lambda^2 430 5]$, this band appears at r and grows brighter to the last fraction at s The substance to which it is due is called Ga Lastly, at $\lambda 456$ [1/ λ^2 481] appears a deep violet band beginning at about o and brightening as we proceed lower down. In some samples of ytterbia, supposed to be pure, this band is in tensely brilliant, but it is absent in a specimen received from Nilson and considered by him to be perfectly pure Hence it is probably due to another new body which may be provisionally named Sy

It must be remarked that the writer's fractionations have been carried far beyond the limits shown in the diagram Fractions above a and below s afford evidence that the process of differentiation has not yet reached its utmost limit.

On the left side of the diagram will be seen chemical symbols attached to some of the spectra. Thus the top spectrum, A, is the one shown by samarium. At D is the spectrum of Marignac's Ya, or gadolinium. It shows the spectrum of mosandrum, and L that which is generally pronounced to be pure yttrium. A careful study of this diagram will lead the observer to conclude that samarium, gadolinium, mosandrum, and yttrium are not true chemical elements but compounds, or perhaps very intimate mixtures, of certain simpler bodies. For these bodies the name 'meta-elements' is proposed (W. Crookes,

B A Birmingham Meeting, C. N 54, 155, Krüss a Nilson, B 20, 2134 and C N 54, 71, 85, distinct substances which he names Za, $Z\beta$, and 135, 142, 154, 165, 172, Marignac, Archives des 'new yttria' (C R 103, 627) It is possible

FIG 14.—Phosphorescence-spectra of components of 'Old Yttria.'



The scale is $\frac{1}{\lambda^2}$

Sciences Physiques, 16, No 5 and C N 57, W. | that Zα is G8, and that Gβ and Zβ are identical, though de Boisbaudran now regards the latter De Boisbaudran likewise finds yttrium to | body as terbia (C R 102, 395, 902)

The right of the 'new yttma' to bear this name is in the highest degree questionable Boisbaudran assigns to it an atomic weight close upon 89, and states that it has a characteristic spark-spectrum but gives no phosphorescence spectrum either in the radiant matter tube or by his reversion-process It evidently cannot be regarded as the old yttrium freed from impurities, since the purest specimens of such yttrium give a phosphorescence spectrum in vacuo of such remarkable intensity that it cannot be due to mere traces of impurities Ga, GB, &c, can no more be spoken of as impurities in old yttrium than can neodymium and praseodymium (as suming them to be elementary) be viewed as im purities in old didymium

Marignac's Yais probably a compound writer recognises in it two at least of the con-

stituents of yttrium, GB and GC

A E Nordenskjöld gives the name oxide of gadolinium (a totally different body from Marignac's Ya or gadolinium) to the mixture of earths in gadolinite which are precipitated by ammonia and oxalic acid, but not by sulphate of potash This mixture consists of yttria, erbia, and ytterbia A very interesting point is that however different the minerals from which it has been obtained, and however the percentage of the rare earths varies, the equivalent weight of the mixture is always approximately the same, viz 261 9 This value is determined by transforming a weighed quantity of the oxide into sulphate by digestion with dilute sulphuric acid, and driving off excess of water and acid by heating to incipient redness (Nordenskjöld, Ö R 102, 795, W Crookes, C N 54, 239)

On the other hand, commenting on this, De Marignac shows that there is sometimes a varia tion of 15 pc in the equivalent weights of these natural mixtures of rare earths (De Marignac,

Arch des Sci Phys 17, No 5)

We have therefore some thirty bodies of which the so called rare metals are composed, or, at least, which they contain, and a variety of facts points to the conclusion that we have by no means come to the end Several even of the new bodies give signs of a capability of further splitting up, if they are examined with sufficient nicety and persistence It is far from unlikely that when the various methods of research known as fractionation have been more generally applied we may have to deal, not with thirty, but with nearer sixty, unknown bodies

But whatever may be the number of these bodies the question must be raised, What are they? Are they each and all independent elements? We have certainly no good a priori grounds for asserting that the number of ele ments now recognised is not capable of consider But before any body can be able extension accepted as simple it should certainly undergo a very severe scrutiny, more severe than any of these newly-discovered bodies has yet undergone The case of didymium is here a warning had been closely examined by some of the ablest chemists in Europe, it had been freed from several foreign bodies, its atomic weight had been established, when a novel mode of examination proved its compound nature

Pending therefore the completion of a series of investigations, chemical and optical, which

will probably occupy several generations of chemists, it may be safest to call these recently observed bodies not, as yet, elements, but quasi or meta elements Our notions of a chemical element have been enlarged, hitherto the ele mental molecule has been regarded as an aggre gate of two or more atoms, and no account has been taken of the manner in which these atoms have been agglomerated. The structure of a chemical element s certainly more complicated than has hitherto been supposed reasonably suspect that between the molecules which we are accustomed to deal with in chemical reactions, and the component or ultimate atoms, there may intervene sub molecules, sub aggregates of atoms, or meta elements, differing from each other according to the positions which they occupy in the very complex structures commonly known as didymium, yttrium, and the

METAMERISM This term is generally applied to those cases of isomerism wherein compounds show identity of elementary composition, but belong to different types or classes (v Iso-

METEORITES As

As regards composition, meteorites have been divided into two classes, those which consist for the most part of metals only, and those which are chiefly composed of silicates, sometimes accompanied by unoxidised iron and nickel Iron and nickel are the principal constituents of those meteorites which are mainly metallic The quantity of Fe varies from 80 to 95 pc, and of Ni from 6 to 10 pc Co occurs in many meteorites, varying from a mere trace to 2 or 3 pc, the other metals found in small quantities are Sn, Mn, Cr, and Cu, small quantities of Fe Ni phosphide, and also carbide, phosphide, silicide, and sulphide of Fe are also frequently found in metallic meteorites The silicates which form the chief constituents of meteorites of the second class are silicate of Al, Ca, and Na (labradorite), silicate of Ca and Mg (augite), and silicate of Fe and Mg (olivine) These silicates are often accompanied by nickel and iron, also by iron pyrites, and sometimes by chrome iron, and magnetic oxide of iron

M M P M.

METHACRYLIC ACID C.H.O. 1 e CH₂ CMe CO₂H a Methyl acrylic acrd [16°], (160 5° 1 \forall) S G 20 1 0153 (Bruhl, B 14, 2800) $\mu_{\rm D} = 1\,4314$ R_{∞} = 35 07 Occurrence - In small quantity in Roman oil

of chamomile (Kopp, A 195, 82)

Formation — I Obtained as ethyl ether by the action of PCl₃ on oxy isobutyric ('dimethoxalic') ether CMe₂(OH) CO₂Et (Frankland a Duppa, C J 18, 133, A 136, 12, Paul, A 188, 52) -2 By the action of fuming HBr on citraconic acid, mesaconic acid, or citraconic anhy dride, the resulting brome pyretartaric acid being boiled with cone NaOHAq (Fittig, A 188, 95, B 10, 517) -3 By boiling citra and mesa chloro pyrotartaric acid with alkalis (Prehn, A 188, 42) -4 Together with oxy-isobutyric acid, by boiling a brome isobutyric acid (1 pt) with water (25 pts.) (Thomson, A 200, 86)

Preparation - Citraconic anhydride is mixed with a saturated solution of HBr (2 vols) at 0°. In a few days a mass of crystals of citra-bromo-pyrotartaric acid is got These are collected, boiled with Na₂CO₃, acidified with HCl, and dis-The distillate is neutralised by CaCO, filtered, evaporated to dryness, and mixed with HCl Methacrylic acid separates as a light oil

(Fittig a C Kolbe, J pr [2] 25, 372)
Properties —Long prisms (from water), with strong but not unpleasant odour V sol water,

v e. sol alcohol and ether

Reactions—1 Bromine forms di-bromo iso-butyric acid—2 Potash fu uon gives hydrogen, formic acid, and propionic acid (F a D) 8 Sodium-amalgam reduces it to isobutyric acid—4 Cone HIAq forms, in the cold, iodoisobutyric acid crystallising in tufts of prisms -5 Methacrylic acid dissolves easily in fuming HBr even at 0°, the solution, after some time, depositing a crystalline addition product and a thick oil (Paul, B 9, 122) -6 Bromins forms CH,Br CBrMe CO,H -7 On contact with cold conc HClAq or by heating at 130°, it is con verted into an amorphous (? polymeric) modifi cation The ammoniacal solution of this sub stance gives white pps with Ba and Ca salts is not altered by conc H₂SO₄ and HNO₃ (Fitting a Engelhorn, A 200, 70)—8 Hypochlorous acid forms chloro oxy isobutyric acid [107°] (c 235°) (Melikoff, Bl [2] 41, 311)

Salts - CaA'₂ tufts of long needles, v sol Appears to change on keeping to a salt water of the polymeric acid (v Reaction 7) -AgA' needles (from boiling water), scarcely affected by light Suddenly decomposes at 100°

Constitution -Inasmuch as the di bromo iso butyric acid, formed by the addition of bromine, is converted by boiling water into a bromo oxy butyric acid that can be reduced to a oxy isobutyric acid, (CH₃)₂C(OH) CO₂H, it is clear that methaci ylic acid is not CH CHMe CO,H but CH, CMe CO H

References - Bromo and Chloro METH ACRYLIC ACIDS

METHACYL BROMIDE v BROMO ACI TONE METHÆMOGLOBIN v H FMOGLOBIN METHAMIDO v METHYL AMIDO

METHANECH, Marshgas Methylhydride Light carburetted hydrogen Mol w 16 (-155° to -160) (-131°) at 6.7 atmospheres. -73.5° SG (air = 1) 553 (Regnault, C R 36,676) SG (liquid) $415 \text{ at } -164^{\circ} \text{ (Olszewski, } P [2] 31,58)$ 8 H 593 (R) $\mu_0 = 1\,000412$ (Croullebois, C R 67, 692) H F p 21,750 H F v 21,170 (Thom sen, Th) HCp 213,500 (Berthelot, A Ch [5] 23, 179) S 05449 at 0° (Bunsen, A 93, 18) S (alcohol) 523 at 0° Critical temperature -73 5° (Wroblewsky), -99 5° (Dewar, P M [3] 18) Critical pressure 56 8 atmospheres [3] 18) (Wroblewsky)

Occurrence - The bubbles of gas given off by decaying vegetable matter in stagnant pools con sist of marsh gas, CO2, and nitrogen escapes into coal mines, where it is known as fire damp, since it forms an explosive mixture It escapes from the earth in various places, as in Italy, North America, and especially at Baku on the Caspian It occurs among the products of distillation of wood, peat, coal, and bituminous shale, constituting 35 to 40 pc of coal gas Methane occurs also in the intestinal gases It occurs also among the products of the passage of ethylene (Norton a Noyes, Am 8,

362) and other gases through a red hot tube. The gaseous product obtained by heating ethylene at 400° contains 36 p c methane and 40 p c.

ethane (Day, Am 8, 153)

Formation —1 By the action of potassium. amalgam on CCl4 in presence of water (Regnault) 2 By passing a mixture of CHCl, or CCl, and hydrogen through a red-hot tube (Berthelot) -By the action of powdered zinc on chloroform dissolved in aqueous alcohol (Sabanejeff, B 9, 1810) -4 By exposing a mixture of CO and hydrogen to the action of electricity in an induction tube (Brodie, Pr 21, 245) -5 By the action of water on zinc methide (Frankland) -6 By the action of sodium on MeI in presence of ether (Wanklyn a. Buckersen) —7 In small quantity by passing a mixture of CS₂ and H₂S over red hot copper (Berthelot, A Ch [3] 53, 69) 8 By heating \tilde{CS}_2 with PH I at 130° (Jahn, \dot{B} 13, 127) -9 Among the products of the dry distillation of barium formate (Berthelot, J 1857, 426) -10 By distilling crystallised sodium acetate (2 pts) with KOH (2 pts) and quicklime (3 pts) (Dumas, A Ch [2] 73, 92) Von Schlegel (A 226, 140) recommends 1 pt of sodium acetate and 2 pts of soda lime (cf Schorlemmer, C N 29, 7) -11 When river mud is added to a solu tion of calcium acetate a slow evolution of a mixture of methane (2 vols) and CO2 (1 vol) occurs, calcium carbonate being left Calcium lactate undergoes a similar fermentation, the gases being evolved in the same proportion (Hoppe Seyler, H 11, 561)

Preparation -By the action of the copperzinc couple on an alcoholic solution of Mel, the escaping gas being well washed by a scrubber containing a further quantity of copper zine (Gladstone a Tribe, C J 45, 154)

Properties — Colourless gas V sl sol. ter Much less soluble in alcohol than water ethane Its illuminating power is slight (cf L T Wright, C J 47, 200) May be liquefied by combined cold and pressure (Cailletet, J 1877, 221) Methane is not absorbed by aqueous KOH or by ammoniacal cuprous chloride When compressed with water below 0° under a pressure of 30 atmospheres it forms a crystalline hydrate, the critical temperature of which is 21 5° (Villard, C R 106, 1602, 107, 395)

Reactions —1 When passed through a red-

hot tube it is for the most part unaffected, buta little naphthalene is formed Electric sparks partially convert it into carbon, hydrogen, and acetylene (Berthelot, C R 67, 1188) When passed over a red hot palladium spiral it is decomposed, if dry, into carbon and hydrogen, and, if moist, into CO and hydrogen (Coquillon, C = R = 86, 1197) —2 It is not attacked by sulphuric acid, by nitric acid, by a mixture of hot cone H.SO, and HNO, by POl, or by chlorine in the dark -- 3 A mixture of chlorine (2 vols) with methane (1 vol) when exposed to sunlight presently explodes The explosion may also be brought about by an electric spark If the mixture be first diluted with CO, and then exposed to sunlight, quiet chlorination takes place, and if excess of chlorine is present chloroform and CCl, are formed A mixture of methane (1 vol) and chlorine (1 vol) exposed to diffused daylight gives methyl chloride In presence of moisture, chlorine forms HCl, CO2, and CO.-

4 A mixture of aur and methane passed over a red-hot platinum spiral yields formic acid (Coquillon, C R 77, 444) -5 When mixed with nitric oxide and fired by an electric spark CO₂ and oxygen are among the products (Cooke, C N 58, 130)

Constitution —That the four atoms of hy drogen in methane are of equal value may be inferred from the existence of only one set of methyl compounds The same thing may be

shown thus

From CHHHI we may obtain, by treatment with KCy, an acetonitrile CHHHCy which we may call 'a' From this we can obtain CHHH CO₂H, CHHCl CO₂H, CHHCly CO₂H, and 'β' acetonitrile CHHCyH successively But from CHHCy CO H we can obtain malonic ether CHH(CO₂Et)(CO₂Et), and thence we can get CHCl(CO₂Et)(CO₂Et), CHCy(CO₂H)(CO₂H), and '\gamma' acetomtrile CHCyHH successively The three acetomtriles '\alpha' '\beta', and '\gamma' are then found to be identical, hence three at least of the atoms of hydrogen in methane are of equal value The fourth acetonitrile might probably be obtained from CH(CO,Et), via CCl(CO,Et), and CCy(CO,H), (Henry, C R 104, 1106) Since co Coc, H, the product of the action of

 $co<_{OEt}^{Cl}$ on isobutyl alcohol, is the same as

 $CO < {OEt \atop OC_4H_9}$, obtained from $CO < {Cl \atop OC_4H_9}$ ethyl alcohol, the carbonyl group is united to two atoms of hydrogen of equal value Now from aldehyde CO CH. we may obtain

Cl > 0 < H whence silver propionate forms $^{C_3H_5O}_{AcO}>^{C}<^{H}_{CH_3}$ But from aldehyde we

may also obtain $_{C_3H_3O}$ $\overset{Cl}{O}$ > $C < \overset{H}{CH_1}$ whence silver acetate yields $_{C_3H_3O}$ > $C < \overset{H}{CH_1}$

These two acetyl propionyl derivatives of ortho aldehyde are found to be identical, hence the two atoms of hydrogen in methane which are displaced by oxygen in forming carbonyl are of equal value It follows that there are two pairs of equivalent atoms of hydrogen in methane (Geuther, A 205, 203, 225, 290) And since Henry has shown that three of the atoms of hydrogen in methane are equivalent, it follows that the fourth 18 so also

References - Tetra Bromo , Bromo 1000, Bromo-nitro , Chloro iodo , Chloro-nitro , and TETRA 10DO-, METHANE, BROMOFORM, CHLORO FORM, IODOFORM, and METHYL, METHYLENE, and In fact, all organic METHENYL COMPOUNDS compounds may be regarded as derivatives of Methane (Kekulé)

METHANE CARBOXYLIC ACID 15 ACETIC

Methane dicarboxylic acid is Malonic acid Methane tricarboxylic acid C,H4O's ve CH(CO,H), Formyltricarboxylic Methenyl tricarboxylic acid

[29°] (200 m 8 G 19 700e Ethyl ether OH(CO₂Et), [29°] (258°) at 760 mm (195°–205°) at 140 mm SG 18 1·100 From sodium malonic ether, benzene and OlCo, Et (Conrad a Guthzeit, A 214, 81; B.

12, 1286, cf Claisen, B 21,8897, 8567) Colour less oil V sol alcoholor ether. In a freezing mixture, it solidifies to long needles or prisms According to Michael (J pr [2] 87, 473) it dissolves readily in dilute NaOH forming CNa(CO,Et)3, which may be crystallised

Reactions —1 With aqueous KOH at 100° it forms HOEt, K₂CO, and potassic malonate — 2 Dilute H2SO, and alcoholic NaOH at 0° also form malonic acid, so that a salt of the acid CH(CO₂H), has not been obtained -3 Chlorine

forms CCl((CO₂Et)₂ (Conrad B 14, 618)

Anilide of the di-ethyl ether

CH(CO₂Et)₂(CONHPh) [124°] From sodiummalonic ether and an alcoholic solution of

phenyl cyanate (Michael, J pr [2] 35,452)
Nitrile of the di-ethyl ether v Cyano

MALONIC ETHER

METHANE PHOSPHONIC ACID v METHYL

METHANE - TRI - QUINOLYL - HYDRO -IODIDE v Quinoline iodoform

METHANE SELINIC ACID v SELENIUM ORGANIC COMPOUNDS

METHANE SULPHINIC ACID CH, SO, 16 CH₃ SO₂H From ZnMe, and SO₂ (Hobson, A 106, 287) The aqueous solution of the acid soon decomposes with deposition of sulphur -CaA'₂ (dried at 100°) amorphous —BaA'₂ (dried at 100°) cubes, v sol water, insol alcohol — MgA'2aq (dried at 100°) — ZnA'2 amorphous

Derivative -Tri chloro methane sulphinic

Methane di-sulphinic ether v METHYLENF DIFTHYL DISULPHON

METHANE SULPHONIC ACID CH.SO, 1.6

Formation -1 By the oxidation of di methyl trısulphide (Cahours, A. Ch. [3] 18, 258), or of dimethyl disulphide (Muspratt, A. 65, 251) —2 By oxidising methyl sulphocyanide with nitric acid (S G 125) -3 By treating tri chloro methane sulphonic acid with sodium amalgam (Kolbe, A 54, 174)—4 By heating MeI with aqueous K₂SO₃ at 120° (Colman, A 148, 101)

Properties—Syrup which decomposes above

Potash fusion forms K2CO3, hydrogen,

and K_2SO_3 (Berthelot, J 1869, 336)

Salts—NH,A' thin trimetric plates (from absolute alcohol)—LiA'aq—(NaA'),NaI (Colman)—KA' (dried at 100°)—KHA'; (dried at 100°)—CaA'; S 71 at 20° (Nithack, A 218, 284)—SrA',aq S 83 at 22°—BaA',2aq v e sol water, insol alcohol -MgA'210aq -PbA'2aq

-CuA', 5aq -AgA'

Chloride CH, SO, Cl (160°) (N) SG

151 From the acid and POl, (Carius, A 114, 142) Not attacked by H.S. by chlorine, or by KCy (McGowan, J pr [2] 30, 280) Decomposes aqueous ammonia with evolution of nitrogen

Amide CH, SO₂NH₂ Formed by passing NH₂ into a solution of the chloride in ether. Prisms (from benzene containing alcohol)

Anilide CH, SA, NHPh (from alcohol) (McGowan) Large plates

Derivatives v Chloro-, and Chloro-Bromo-METHANE SULPHONIC ACID

Methane disulphonic acid CH₄S₂O₆ CH₂(80₂H)₂ thronic acid Methylene drsulphonic acid.

Formation.-1. A product of the action of

SO₂ on ether (Liebig, A 13, 35, Wetherill, A 66, 122, Strecker, A 100, 199)—2 From Et₂SO₄ and SO₂ (Hubner, A 223, 208)—3 By the action of hot fuming H2SO, on acetonitrile, acetamide, or sulpho-acetic acid (Buckton a Hofmann, A 100, 133, C J 9, 241)—4 Together with sulpho-acetic acid, by the action of CISO, H on acetic acid (Baumstark, A 140, 82) 5 By heating lactic acid with fuming H₂SO₄ (Strecker, A 118, 290) —6. From methylene todide and K₂SO₂ (Strecker, A 148, 90) —7 By heating chloroform with aqueous K2SO2 at 180° (Strecker) — 8 From CCl, SO, K, water, and K, SO, at 125° (Rathke, A 161, 152) — 9 By oxidising CH₂(SCy)₂ with HNO₃ (Lermontoff, B 7, 1282)

Properties - Very deliquescent reedles attacked by chlorine or by nitric acid

Salts —(NH₁)₂A" trimetric crystals, m. sol cold water —K₂A" needles S 7 1 at 22° —BaA" 2aq pearly tables —PbA" 2aq prisms, v sol water, insol alcohol -CuA" 5aq -Ag,A" thin plates

Derivative v Bromo methane disulphonic

Methane tri-sulphonic acid CH₄S₃O₉ ie CH(SO₃H), Obtained by heating CH,O SO,K (1 pt) with fuming H,SO, at 100° (Theilkuhl, A 147, 134) Formed also by the action of aqueous K₂SO₃ at 100° on CH₂C(NO₂)(SO₃K)₃ or on CCl₂(NO₂) (Rathke, A 167, 219) Long needles, v e sol water and alcohol—K₂A'''aq small v e sol water and anomor—aph aq prisms—Ca₂A'''₂12aq small prisms, v sol water, insol alcohol—Ba₂A'''₂9aq plates Not decomposed by HCl—Pb₂A'''₂O₂

METHANE THIOSULPHONIC ACID

Methyl ether C2H6S2O21e CH3 SO2 SCH2 Dimethyl disulphoxide Obtained by warming dimethyl disulphide with nitric acid (SG 12) diluted with four times its volume of water (Lukaschevitch, Z 1868, 641) Oil Readily

oxidised by HNO, to methane sulphonic acid METHANTHRENE $C_{15}H_{12}$ [117°] An is meride of methyl naphthalene obtained, together with other products, by distilling podocarpic acid with zinc dust (Oudemans, B 6, 1125) The product is crystallised from alcohol and sublimed White laming with violet fluorescence It boils above 860° V e sol. boiling alcohol, CS, and HOAc

Picric acid compound

C12H12C2H2(NO2)2OH [117°] Slender orange needles

[187°] Methanthrene-quinone C, H, O, From methanthrene and CrO, in HOAc Minute trimetric laminæ May be distilled Insol water, sl sol ether, v sol alcohol Reduced to a hydride by aqueous SO, METHAZONIC ACID C2H4N2O, s.c.

NO CH₂)₂O? [c 60°] The sodium salt is formed by acting on nitro methane with alcoholic NaOH, the resulting crystalline pulp being heated on the water bath The upper (alcoholic) layer is poured off, and the lower layer deposits sodium methaconate on cooling I is dissolved in water and reppd by alcohol (Friese, B 9, 804) Ac cording to Lecco (B 9, 705) it is best to add dilute H,80, and shake with ether If the ether is deied with Na SQ and shake with ether if the ether is dried with Na₂SO₄ and evaporated over H₂SO₄, it leaves methazonic acid as large crystals, which may be recrystallised from benzene. It is v. sol

water, alcohol, and ether, m sol benzene, insol petroleum naphtha The Na salt crystallises from alcohol in long prisms METHENYL-AMIDINE v Formamidine

METHENYL-AMIDOXIM v FORMAMIDOXIM METHENYL-AMIDO-o-CRESOL CaH, NO + 6. $C_sH_s(CH_s) < N > CH [3]$ [89°] (200°) **Co**lourless crystals Prepared by the action of formic acid on amido-o cresol (Hofmanna Miller,

B 14, 570)

Methenyl-amido p-cresol CaH, NO : 6.

 $G_0H_3(CH_3) < N > CH [5] [46^\circ]$ Formed from amido p cresol by distillation with formic acid (H a M) Crystals

METHENYL (α) AMIDO NAPHTHYL MER-CAPTAN C₁₀H₄<^NSCH [46°] Formed by heating formyl (a) naphthylamine with sulphur Colourless oily fluid Insol water Volatile Base -B'2H2Cl2PtCl4 steam yellow needles (Hofmann, B 20, 1799, 2265)

METHENYL-AMIDO-PHENOL C,H,NO .. $C_{\bullet}H_{\bullet} < N > CH [30.5^{\circ}] (182.5^{\circ}) V D (H=1)$ 112 5 (cale 119) Obtained by boiling formic acid with o amido phenol (Ladenburg, B 10, 1123) Prisms Hot cone HClAq decomposes it, forming o amido phenol

METHENYL-AMIDO-PHENYL MERCAP. TAN C_7H_4NS 4.6 [1 2] $C_6H_4 < N > CH$ (230°) Colourless fluid Sparingly soluble in water, easily in alcohol and CS₂. Has decided basic properties Heavier than water Volatile with steam Isomeric with phenyl mustard oil

Preparation -1 By reduction of the chloro derivative (vol 11 p 78) with tin and HCl or with HI -2 By the action of formic acid on amido phenyl mercaptan (Hofmann, B 13, 14) 3 Formed together with aniline, methyl aniline, and a base C₈H₇NS₂, by boiling di methyl aniline with sulphur (Mohlau a Krohn, B 21, 59)

Properties -Oil, smelling like quinoline and having a bitter taste It is related to thiszole as quinoline is to pyridine The sulphur cannot be displaced by the action of lead hydrate or even by heating with copper to 250° On fusion with KOH it gives formic acid and amido phenylmercaptan PCl, at 180° forms the chloro deri vative CeHe(NS)CCl

Salts—(B'HCl),PtCl, sparingly soluble tables, or needles—(B'HCl)AuCl,—B',H,FeCy, Methylo-sodide C,H,NSMeI [210°]; needles, si sol cold alcohol, v sol hot water

General character -This base stands in the same relation to quinoline as thiophene stands to benzene In consequence of this analogy the base and its derivatives exhibit great similarity in properties with the corresponding quinoline compounds thus the boiling-points of the methenyl- and ethenyl-o amido phenyl mercaptan do not differ much from those of quinoline and methyl-quinoline, and they form crystalline picrates and uncrystallisable chromates They also form colouring-matters analogous to the cyanines (obtained by the action of alkalis upon a mixture of the alkylo-iodides of quinoline and methyl quinoline) Thus by boiling an aqueous solution of the amylo-iodides of methenyl- and ethenyl amido-phenyl mercaptans with NH₃, a red colouring matter C₂₃H₃₁N₂S₂I is obtained which crystallises in four sided violet red plates with green reflex, sol hot alcohol, sl sol cold al cohol, insol water Neither of the amylo iodides when treated separately, in the same way, gives any colouring matter In a similar manner to the amylo rodides, the mixed methylo rodides give a compound crystallising in reddish-golden plates, sol alcohol with a scarlet red colour Similar colouring matters are also obtained from the corresponding derivatives of amido naphthyl mercaptan, or from the latter derivatives cor. jointly with those of amido phenyl mercaptan, or from those of amido phenyl-mercaptan conjointly with those of quinoline and methylquinoline All the above products are stronger colouring matters than the cyanines (Hofmann, B 20, 2262)

Derivatives v Amido-, Chioro, and Nitro-METHENYL-AMIDO PHENYL-MERCAPTAN

METHENYL-0-AMIDO-PHENYL-MERCAP-TAN ω -CARBOXYLIC ACID $C_{\bullet}H_{\bullet} < N \\ S > C CO_{\bullet}H$

Formation -1 By the action of cold alco holic caustic potash upon amido imido ethenylo-amido phenyl mercaptan

 $C_{\bullet}H_{\bullet} < N > C(NH_2)NH$, ammonia being eliminated -2 In small quantity by oxidation of ethenyl-o-amido phenyl mercaptan

C.H. N C CH3 with cold aqueous KMnO. Properties - White needles Sol water and alcohol It very readily splits off CO2 giving methenyl amido-phenyl mercaptan (Hofmann,

B 20, 2256) METHENYL AMIDO-TOLYL MERCAPTAN

 $C_0H_3(CH_3) < N > OH [1 \frac{4}{3}] [15^{\circ}]$ (255°) Pre pared by boiling p-amido m-tolyl-mercaptan with formic acid (Hess, B 14, 492) Sol alcohol and ether Weak base forming unstable salts -(B'HCl) PtCl, needles
METHENYL AMIDOXIM v FORMAMIDOXIM

METHENYL-AMIDO XYLYL MERCAPTAN

 $C_{\bullet}H_{\bullet}(CH_{\bullet})_{\bullet} \stackrel{N}{<} CH$ From the thio-formyl derivative of u m xylidine $C_0H_3Me_2(NH CSH)$ by oxidising with alkaline K_3FeCy_6 (Gudeman, B21, 2549) Heavy oil

METHENYL BROMO - TOLYLENE - o - DI-

AMINE $\begin{bmatrix} 1 & 4 & 2 \\ 3 & 3 \end{bmatrix}$ $C_6H_2(CH_8)(Br) < NH > CH$

Obtained by heating bromo-tolylenediamine with formic acid (Hubner a Schupp haus, B 17, 776) Fine colourless needles Sol alcohol, ether, and acetone, sl sol water and benzene

Salts —B'HCl colourless soluble needles — B'H₂SO₄aq long needles —B'HNO₃ sparingly soluble colourless needles — B'2H2Cl2HgCl2 needles -B'2H,Cl2PtCl4 orange crystalline pp -B',H₂Cr₂O₇ glistening B'C₆H₂(NO₂)₃OH this pic needles [229°] red necules this picrate forms yellow

METHENYL-TRICARBOXYLIC ACID

METHAME-TRICABBOXYLIC ACID

METHENYL FLUORIDE CHF. Fluoroform. VD. 250 (calc 244) S (alcohol) 5

Formed by warming a mixture of iodoform (2 pts). chloroform (1 pt), and silver fluoride (2 pts) (Meslans, C R 110, 717) Colourless gas, condensing at 20° under 40 atmospheres' pressure Smells like chloroform, and burns with blue flame forming HF Sl sol water, chloroform, and benzene Alcoholic KOH yields KF and potassium formate

METHENYL DI PHENYL-DIAMINE v DI-PHENYL FORMAMIDING

METHENYL - o - PHENYLENE - DIAMINE $C^eH^*{<}_{\rm NH}^N{>}CH$ Anhydro-formyl phenylene [167°] (above 360°) dıam**ıne** Prepared by heating ortho phenylene diamine for 5 or 6 hrs with formic acid The yield is nearly theoretical (Wunds, B 11, 826) Large crystals

Monacidic base — (B'HCl)₂PtCl₄ — (B'HCl)AuCl, METHENYL TRI PHENYL TRI KETONE TRI BENZOYL METHANE

METHENYL DI TOLYL-AMIDINE v. DI-TOLYL FORMAMIDINE

METHENYL-TOLYLENE o DIAMINE

 $C_{e}H_{s}(CH_{s}) < N > CH [1 2 3] [143^{\circ}]$ Obtained by reduction of methenyl bromo tolylene o di amine (Hubner a Schupphaus, B 17, 777) Colourless glistening needles (from benzene) e sol water and alcohol

Salts -B'HNO₃ long soluble needles -B',H,Cl,PtCl, 3aq sparingly soluble orange needles

Methenyl-tolylene-diamine

C₆H₃(CH₃)<NH>CH [1 3 4] [c 101°] From the diamine and formic acid (Ladenburg, B 10,

1123) —B'₂H₂PtCl_s yellow prisms
METHIONIC ACID v METHANE DISULPHONIC ACID

METHOXY-compounds v Methyl derivatives of Oxy- compounds

METHRONIC ACID C.H.O. v.e. C.H.O(CO.H). C(CO₂H) CH OMe O C CH₂ CO₂H (Knorr, B 22, 152)

Dr methyl furfurane dicarboxylic acid Sylvans carboxyacetic acid Pyrotritaric carboxylic acid

[205°] (F), [207°] (P)

Formation -1 By heating equimolecular weights of aceto acetic ether, Ac,O, and sodium succinate, and saponifying the resulting mono ethyl methronate C₆H₆O(CO,Et)(CO,H) with baryta (Fittig, A 250, 173, 182) 2 By treating a mixture of glyoxal and aceto acetic ether with a concentrated aqueous solution of ZnCl2, and extracting the product with aqueous KOH (Polo nowsky, A 246,6, Fittiga Hantzsch, B 21,2135, 3189)

Properties — Needles (from water), v e sol. alcohol, m sol ether and HOAc, m sol hot, v. sl sol cold, water, almost insol CHCl, and CS2 The aqueous solution gives no colour with FeCl, It is not attacked by reducing agents

Reactions -1 On heating it gives off carbonic acid gas leaving methyl-furfuryl acetic CH CH

[188°]. — 2 Dilute acid | ÖMe O Ö CH₂ CO₂H

HOlAq at 200° gives CO₂ and acetonyl acetone. Salts—(NH₄)₂A" jaq small needles— CrH₂A"₂: heavy crystalline pp nearly insol.

hot water —CaA" 2aq —BaA" 2aq needles (P) -BaA" amorphous (F) -BaH2A" needles, more soluble than the Ca salt (F) -Ag₂A"aq bulky white pp

[98°]; Mono-methyl ether MeHA"

needles —AgMeA" white pp (P)
Di methyl ether Me₂A"

Mono-ethyl ether EtHA' [76°] Pre pared as above Long pointed needles, v sol alcohol, ether, chloroform, and benzene, m sol CS2, sl sol water - Ca(EtA")2 2aq needles or prisms—Ba(EtA"), 28q needles, v sol hot, sl sol cold, water—AgHA" white matted needles

Diethyl ether Et, A" (300°-805°) (F)

Phenyl hydraside C, H, N, O, ve

 $C_8H_8O_4$ $N_2HC_6H_5$ [212°] (F)

Phenyl hydraside of the mono-ethyl sther C₁₈H₁₈N₂O₄ cold aqueous alkalıs [134°], crystalline Insol

METHRONOL C18H20 1.6. CH CH C CHPh CHMe

Phenyl di methyl CH CH C CH, CHMe naphthalene tetrahydride (323°)(cale 82) Formed from phenyl methacrylic acid by heating with H,SO, (40 cc) and water (60 cc) (H Erdmann, A 227, 250) Oil Chromic mixture oxidises it to o benzoyl benzoic acid, acetic acid, benzoic acid, anthraquinone, and

METHYL The radicle CH, The name methyl was also given by Frankland and Kolbe (C J 1, 60) to dimethyl C_2H_6 , now called ethane The methyl derivatives of hydroxylic compounds are described under the compounds of which they are the ethers e g CH₃O C₆H₄ CO₂H, the methyl derivative of oxy benzoic acid is described under OXY BENZOIC ACID

DI-METHYL-ACETAL so called V vol i p 105

METHYL ACETAMIDE v Acetyl derivative of METHYLAMINE

METHYL-ACETANILIDE v Acetyl derivative of MFTHYL-ANILINE

METHYL ACETATE v ACETIC ACID METHYL-ACETIC ACID 18 PROPIONIC ACID Di-methyl acetic acid is Iso BUTYRIC ACID Tri-methyl acetic acid v Valeric acid METHYL-ACETO ACETIC ACID v vol 1 p.

22, vol 11 p 78
METHYL ACETO-ACETATE v ACETO ACETIC

METHYL DI-ACETONAMINE ACETON-

AMINE METHYL-ACETONE v. METHYL ETHYL RE-

Di-methyl acetone v METHYL ISOPROPYL KE-

TONE and DI ETHYL KETONE METHYL - TRI - ACETONE - ALCAMINE v.

ACETONE ALCAMINE METHYL-TRI-ACETONINE V ACETONINES METHYL-ACETO-PROPIONIC ACID v ACE

TYL BUTYRIO ACID METHYL ACETO-SUCCINIC ETHER v ACE-

TYL-METHYL-SUCCINIC ETHER METHYL-ACETOTHIENONE v. METHYL-

THIBNYL METHYL KETONE METHYL - ACETYL - BENZENE v. TOLYL

METHYL REPORT.

Di-methyl-acetyl bensene v. XYLYL METHYL MINTONE

METHYL ACETYLENE v ALLYLENE. Di methyl-acetylene v Butinene

Di methyl-di-acetylene C.H. 2 e CH, C C C C CH, Hexunene [64°] (180°). Formed by oxidising the copper derivative of allylene with alkaline K₃FeCy₆ (Griner, C R 105, 283) Solid, volatile with steam Does not react with ammoniacal cuprous chloride Combines with bromine in the cold, forming C6H6Br4 [44°]

METHYL-ACETYLENE DI QUINOLINE

C21H16N2 20 CH CH OH CH C N CMe C'H' CH CH C Ethulсн с сн сн ene quinoline methyl quinoline [157 5°]. Formed on heating p amido (Py 3) styryl-quinoline with HCl at 150°, and then gradually adding paraldehyde (Bulach, B 22, 289)

DI v METHYL-ACETYLENE-DI-URRA

NMe CH NMe. C₆H₁₀N₄O₄ CO NH CH NH NMe CH NH

CO NH CH NMe CO Glycol-di methyl uril. [210°] Formed by adding HCl to a mixture of glyoxal and methyl urea (Franchimonta Klobbie, R T C 7, 19) Needles, v sol water, msol. ether and ligroin Forms with HNO, a di nitrocompound, which is not decomposed by boiling

with water Di-methyl-acetylene di urea CaHioN4O2 2.6. NH CMe NH

CO Formed by heating di-NH CMe NH methyl diketone with urea in aqueous solution (Franchimont a Klobbie, R T C 7, 251) Prisms or needles, insol ether and CHCl_s, al sol alco-hol Does not melt below 290° Nitrio acid converts it into a nitramine

NH CMe N(NO₂) CO, which crystallises NH CMe N(NO,)/

from alcohol in plates, and is decomposed by boiling water into CO2, N2O, di methyl diketone, and urea

a DI METHYL & ACETYL PROPIONIC ACID v Mesitonic acid

METHYL-ACETYL-PYRROLE @ METHYL-PYRRYL METHYL KETONE

v Methyl-di-acetyl-pyrrolev Methyl-pyrryl-ENE DI METHYL DI-KETONE

METHYL-ACETYL UREA v Acetyl derwatwe of METHYL UREA

METHYL ACRIDINE C, H, N 4.6

C.H. [114°]. Formed by heating C,H

diphenylamine (50 g), glacial scetic acid (30 c c), and ZnCl₂ (85 g.) at 220° for 14 hours The yield is good (32 g) (Bernthsen, A 224, 35) Formed also by heating diphenylamine with acctonitrile at 200° (Bernthsen, A 192, 29) Dimetric crystals, a c=1 2397 (Bernthsen a. Osann, B 19, 427) Aqueous KMnO, at 100° oxidises it very slowly, a product being perhaps quinoline tri carboxylic acid. HNO₂ (S G 183) boiled for 6 hours with methyl acridine (6 g) gives tri-nitrosoridine carboxylic soid, which forms glittering prisms, sparingly soluble in the usual menstrua -B'HOL-B',H,PtOl

Methylo-rodide B'MeI [185°], redneedles from water). Sol hot water, less sol hot alcohol, least sol ether

Methylo-chloride B'MeCl. Decomposes

at 180°-185°.

Methylo-hydroxide B'Me(OH) the methylo rodide by treatment with aqueous NaOH Grey powder, turning green in air Sol. alcohol, but soon decomposes

Methyl-acridine C_sH₄< | N $O_0H_0M_0$

Formed by distilling diamido-di-p tolylphenyl methane PhCH(C,H,MeNH,), with zinc dust (Ullmann, J pr [2] 36, 265) Yellow matted needles Smells aromatic, and causes sneezing V sl sol. water, v sol alcohol, ether, benzene, and hot petroleum ether Its solution in dilute H2SO4 exhibits bluish green fluorescence

Di-methyl-acridine C15H13N & e

CMe, $C_{\bullet}H_{\bullet}Me$ $\begin{bmatrix} 2\\1\\4 \end{bmatrix}$. [128°] Formed

by heating phenyl p toluidine (12g) with HOAc (6 6 g) and ZnCl, (18 g) at 230 (Bonna, A 239, 64) Needles or prisms (from alcohol) Volatile with steam V sol alcohol and benzene — B'HOl yellow needles—B'HI orange reneedles—B'C₈H₂(NO₂),OH brown orystals orange red The sulphate is reddish-brown

Methyl-acridine chloral v TRI CHLORO OXY-

PROPYL-ACRIDINE

DI-METHYL-ACRYLIC ACID & PENTENOIC

TETRA-METHYL ADIPIC ACID C10H18O4 t 6 CO₂H CH₂CMe₂ CMe₂CH₂CO₂H? [210°] product of the action of finely-divided silver on a-bromo-isovaleric ether CHMe, CHBr CO, Et (C Hell a W Mayer, B 22, 52) Snowy-white granules (from benzene), v sol alcohol and chloroform. Forms no anhydride on heating (difference from di-isopropyl succinic acid which accompanies it in its preparation) May be sublimed—BaA" 2aq—SrA" 4aq—S 16 6 at 19°—MgA" 5aq—S 12 5 at 15°—MnA" 3aq—S 5 9 at 25° —NiA" 4aq S (of NiA") 47 at 25° —
CoA" 8aq. S (of CoA") 6 65 at 23° —ZnA' S
195 at 18°.—CdA" 3aq S 2 29 at 81°.—CuA" 8 024 -PbA" S 045 at 18° -Ag.A". S .046 at 18°

METHYL-ESCULETIN v. ESCULETIN. METHYLAL v FORMIC ALDEHYDE METHYLALAGREATINE v ALACREATINE

METHYL ALCOHOL CH, O t e. CH, OH Oxymethane Methyl hydroxide Wood spirit Wood naphtha Mol w 32 (64-8°) (R Schnff, A 220, 99), (65-9°) (Perkin, C J 45, 465), (66-2°) (Zander) S G ¾ 7953 (Brühl), ¼ 79726, ½ 78941 (Perkin), % 8111 (Zander) S V 42.7 (S), 42.6 (Lossen, A 254, 55) µ_e=1 3832 (Brühl) H F p 51,450 (Thomsen), 61,400 (Stohmann, J pr [2] 40, 358) H.F.v. 50,580 (Thomsen, Th). H C 170,600 (Stohmann). M.M. 1 640 at 18.7°. Compressibility. 00010879 at 15° (Dupré, Pr 20, 386) Methyl hydroxide Wood spirit methane

Occurrence.—Free in the juices of plants (Guthseit, J. 1879, 905, Maquenne, O R 101, 1067) and in the aqueous distillate in the fruits ed Heracleum (Guthzeit, A. 177, 844; 240, 248).

Methyl alcohol occurs also in the product of the distillation of wood (Taylor [a.D. 1812], Telloch's Phil Mag 60, 315, Dumas a Peligot, A 15, 1; A Ck 58, 5, 61, 193) and of colophony (Kelbe a. Lwow, B 16, 851) It occurs as methyl salicylate in oil of winter-green (Gautheria procum-

Formation. 1 From methane by chlorinating, and heating the resulting methyl chloride with aqueous KOH for 7 days at 100° Berthelot, 105, 241) The MeCl may also be treated with HOAc and NaOAc at 200°, and the result-ing MeOAc saponified McCl treated with Ag. 80, and H₂SO, at 100° gives HMeSO, whence methyl alcohol can be readily obtained —2 From hydrogen cyanide by reduction with zinc and H2SO4, and treating the resulting methylamine with nitrous soid (Linnemann, Z [2] 4, 284) – 8 By distilling calcium formate (Lieben a. Paterno, G 3, 290, A. 167, 293, Friedel a Silva, C R 76, 1545)

Preparation -The crude watery liquid obtained by the distillation of wood contains methyl alcohol, acetone, acetic acid, methyl acetate, and ammonium acetate It is separated from the tarry products and redistilled, the first tenth of the distillate is mixed with slaked lime and redistilled, a little sulphurio acid is then added, and the liquid redistilled and rectified over quicklime The crude wood spirit thus obtained has a strong aromatic odour and turns brown on keeping. It contains methyl acetate, acetone, di-methyl acetic orthaldehyde CH, CH(OMe), (Dancer, C J 17, 222), allyl alcohol, methyl ethyl ketone, and other ketones (Grodzky a Krämer, B. 9, Methyl alcohol may be obtained from wood spirit by saturating with fused CaCl, and heating on a water bath The residue is a compound of methyl alcohol with CaCl, which when distilled with water is decomposed, giving off the methyl alcohol The distillate is then rectified over quick-lime (Kane, A 19, 164) According to Gould (C J 7, 811) it is best to distil the wood spirit with cone NaOHAq (to saponify MeOAc) and then to dehydrate with K2COs before saturating with CaCl. A better method for obtaining methyl alcohol from wood spirit is to distil the spirit (1 pt) with H2SO4 (1 pt) and potassium oxalate (2 pts), the crystalline di-methyl oxalate is then decomposed by distillation with water, and the MeOH dried over lime (Wöhler, A 81, 376) The oxalate may also be obtained by dissolving oxalic acid, dehydrated at 100°, in boiling MeOH, leaving the solution to cool, and washing the crystals with cold water as long as the filtrate exhibits the iodoform reaction (Erlenmeyer, N Rep Pharm. 28, 624). An alternative method consists in passing HCl into a solution of benzoic soid in wood spirit, distilling, ppg with water the portion collected above 100°, decomposing by boiling for several hours with aqueous NaOH, distilling, and rectifying over quick-lime (Carius, A. 110, 210). The following modification of Wohler's process is recommended by Dittmar a. Fawsitt (Tr. E 38, 509) 100 c.c of wood spirit are digested with 150 g of powdered NaOH, and then distilled on a water-bath, 500 g. of oxalic acid crystals are mixed with 200 c.c. of sulphuric acid, and then 400 c.c. of the alsohol, purified as above, is added, and the whole cautiously heated on a

The methyl exalate thus obtained ' water-bath is thoroughly dried by pressure, and the alcohol regenerated by digestion with water at 70° To dehydrate the alcohol thus obtained, digestion with baryta, lime, and dried copper sulphate is necessary Even when prepared from the oxalate methyl alcohol is not quite pure, as it contains bodies which exhibit Lieben's iodoform reaction It may be freed from these by dissolving in it one tenth of its weight of iodine, gradually adding NaOH until the liquid is distinctly alkaline, and distilling The product, rectified over CaO, has a specific gravity of 81 at 15° (Reg nault a Villejean, A Ch [6] 4, 430, C R 99, Methyl alcohol may also be prepared by saponifying methyl formate (\$\beta\$ pts) with NaOH (2 pts) and water (6 pts) (Grodsk, a Kramer, B 9, 1928, Baidy a Bordet, A Ch [5] 16, 564) Methyl alcohol may be obtained very nearly pure by distilling oil of winter green with potash, and rectifying the distillate over lime

Properties—Colourless mobile liquid, with purely spirituous odour Burns with a pale flame Mixes with water, alcohol, and ether, dissolves fixed and volatile oils and most resins Hence it is much used as a solvent. In aqueous solution it produces intoxication, in concentrated solution it is poisonous. When perfectly dry it dissolves a little CuSO, acquiring a bluish green colour, but it does not dissolve crystallised CuSO, 7aq (Klepl, J. pr. [2] 25, 526). Methyl alcohol is etherined by acetic acid more rapidly and completely than any other alcohol (Men schutkin, Z. P. C. 1, 611). Dittimar a Fawsitt give the specific gravity of mixtures of methyl is specific gravity.

alcohol and water as follows

Pcof	S (r	8.0
CH, OH	at 0°	at 15 96°
0	9998 7	9990 7
10	98429	9826 2
20	97233	96808
30	96057	95 36 7
40	9457	93697
50	928 73	91855
60	90917	89793
70	88687	87487
80	86314	85035
90	83751	82396
100	81015	79589

Older determinations are by Ure (P M [8] 19, 51), Dupre (Pr 20, 336), and Duclaux (A Ch 15] 13, 87) The same observers find the vapour tension of methyl alcohol, measured in milli metres of mercury at 0°, to be

Temp	Tension	Temp	Tension
°o	29 7	40	259 4
10	538	50	409 4
20	94 0	60	624 3
30	158 9	64 96	760 0

(cf Konovaloff, P [2] 14, 40) The following vapour tensions are given by Richardson (C J 19, 762)

Temp	Tension .	Temp	Tension
- 8°3	178	39° 2	285 13
+07	82 06	49 2	370 26
11 2	55 82	59 9	584 24
22 7	108 96	65 7	753 0 5
30 2	155 32		
Vol II	ī.	•	

The specific heat of aqueous methyl alcohol was found by Dupré to be as follows —

	Weight p.c	
Specific	of methyl	Specific
heat	alcohol	heat
9 858 2	60	8017 7
95914	70	7550 0
92658	80	69999
89219	90	64282
84645	100	54325
	heat 98582 95914 92658 89219	heat 80 80 89219 80 80 80 80 80 80 80 80 80 80 80 80 80

Estimation —Pure methyl alcohol does not give Lieben's iodoform reaction with iodine and notash

The amount of methyl alcohol in commercial wood spirit may be estimated by adding 5 c o of the spirit, drop by drop, to 30 g of PI₂ in a flask provided with inverted condenser. The flask is then heated for 5 minutes in boiling water, and the MeI then distilled off by inclining the condenser. The volume of MeI is read off in a graduated receiver 5 c c of methyl alcohol yield 7 19 c c of methyl include (Krell, B 6, 1310, cf Grodzky a Kramer, B 7, 1495, 9, 1928). If it is desired to determine how much of the methyl alcohol is in the form of MeOAc, the spirit may be boiled with standard alkali, and the amount used up in the saponification determined

Bardy and Bordet (A Ch [5] 16,565) modify Krell's process, using only 15 g of PI to 5 cc of wood spirit, but adding 5 cc of aqueous HI subsequently They distil the liquid at %0°-90°, and at the end of the distillation add 5 cc of water and quickly distil The methyl iodide is washed once or twice with water and measured

Di methyl ortho acetic aldehyde or methyl acetal CH₁ CH(OMe), boils at 64° and gives MeI on treatment with PI₂, but it does not react with aniline, so that when the wood spirit is to be used in preparing di methyl aniline, by heating with aniline hydrochloride, the estimation by

PI, will give too high results

The presence of acetone is objectionable in methyl alcohol that is to be used for preparing di methyl aniline. Its amount can be determined by shaking 1 or 2 cc of the alcohol with 20 or 30 cc of normal aqueous KOH, adding 20 or 30 cc of a decinormal solution of iodine, until the solution is clear. The liquid is then acidited with HCl (S G 1025), excess of decinormal sodium thiosulphate added, and the excess determined by titrating back with iodine solution If 1 cc of methyl alcohol be taken, the weight of acetone in 100 cc will be found by multiplying the amount of iodine used up by 7612 (Messinger, B 21, 3366, cf kramer, B 13, 1002, Hintz, Fr 27, 182)

The estimation of methyl alcohol in ethyl alcohol can be effected by oxidation with a standard solution of h₂Cr₂O₂, for 1 pt of ethyl alcohol reduces 4 278 pts of the dichromate in becoming oxidised to acetic acid, while 1 pt of methyl alcohol, in being oxidised to CO₂ and water, reduces 9 224 pts of K₂Cr₂O₂. A solution of 80 g K₂Cr₂O₂ and 150 c c H₂SO₄ per litre is employed, and the unreduced chromate estimated volumetrically (O Hehner, An 12, 25)

When 10 cc of pure ethyl alcohol are shaken with 1 cc of a 1 pc solution of KMnO, at 20°, no reduction takes place for 20 minutes, but if the ethyl alcohol contains crude wood

spirit, decolourisation takes place at once (Haber mann, Fr 27, 663)

Reactions - 1 Passage through a red hot tube yields acetylene and other products (Berthelot, O R 50, 805) -2 In contact with platinum black and air it is oxidised to formic aldehyde and formic acid -8 Heated with ammonium chloride in a sealed tube at 300° it yields mono-, di-, and tri methylamine (Berthelot) 4 Bleaching powder does not yield chloroform (Goldberg, J pr [2] 24, 115) - 5 Potassium gives off hydrogen, forming KOMe -6 When its vapour is passed over heated potash, hydrogen is given off, and potassium formate, oxalate, and carbonate are successively formed -7 Conc H SO4 forms HMeSO4, which, when heated with excess of methyl alcohol, yields di When distilled with excess of methyl oxide H₂SO₄ di methyl sulphate passes over —8 Con verted into methyl chloride by treatment with HCl, with PCl₈, or with S₂Cl₂ The joint action of H2SO4 and HBr gives rise to methyl bromide and ethyl bromide (Niemilovitch, M 10, 820) — 9 SOCl₂ forms MeSH, Me₂SO₄, MeCl, and other products (Carius, A 111, 93) —10 SO₅ forms CH(OH)(SO₂H)₂ (Max Muller, B 6, 1031) — 11 When acidulated with 5 pc sulphuric acid and submitted to electrolysis it forms CO2, CO, methyl formate, methyl sulphate, and methylal (Renard, C R 80, 236) -12 Distillation over heated zinc dust splits it up into CO and hydrogen, a very little methane being also formed (Jahn, B 13, 983, M 1, 378) — 13 Zinc chloride forms CH4, water, Me2O, hexa methylbenzene, and traces of propylene, butylene, and other hydrocarbons (Le Bel a Greene, C R 87, 260, 89, 413) -14 Aldehyde (1 vol.), MeOH (2 vols), and HCl form CH3 CH(OMe)2 (Claus a Trainer, B 19,3004) -15 Not affected by B aceti growing in solutions containing it (Brown, C J 49, 177) -16 Converts m and p diazo benzoic acid into C6H4(OMe) CO2H, while o diazo benzoic acid only gives benzoic acid (Griess, B 21, 978) -17 When heated with hydrochlorides of aro matic bases (e.g. aniline, xylidine, piperidine) it often displaces hydrogen in the nucleus by methyl (Hofmann, B 15, 2895, Ladenburg, B16, 2057) -18 Unlike EtOH, it hardly reacts when heated with phenol and ZnCl₂ (Auer, B 17, 669) -19 Unlike butyl and amyl alcohols, it does not form a homologue of benzene when heated with benzene and ZnCl₂ at 270° (Gold schmidt, B 15, 1066) — 20 ClCONH, forms methyl allophanate NH2.CO NH CO2Me [208°] (Gattermann, A 244, 40)

Metallic derivatives - KOMe tained by dissolving K in methyl alcohol-(KOH)_s(MeOH)_s or (KOMe)_s(MeOH)₂ 3aq [c 110°] Obtained by evaporating a solution of KOH in methyl alcohol (Göttig, B 21, 1882) Large elastic plates, somewhat heavier than water, on which they move about rapidly, decomposed - $-(NaOH)_{s}(MeOH)_{s}$ Obtained by dissolving (NaOMe), MeOH aq NaOH in dry MeOH and evaporating Crystalline mass, which moves about on the surface of water while decomposing and dissolving — NaOMe 1 aq Obtained by evaporating a solution of NaOH in not quite dry methyl alcohol (Gottig, B 21, 561) -NaOMe(MeOH), (Fröhlich, A 202, 295) CO passed over NaOMe at 160°

forms acetic acid CO passed into a hot mixture of NaOMe and NaOAc forms propionic acid (Geuther a Fröhlich, A 202, 312) When dostilled with the Ba salt of a carboxylic acid it displaces the carboxyl by hydrogen Thus succinic acid may be converted into propionic acid (Mai, B 22, 2135) — TIOMe From TIOEt and excess of MeOH (Lamy, J 1864, 466) — (Ba(OMe)₂)₂BaO₂H₂ aq White nacreous plates, obtained by evaporating at 135° a solution of BaO in MeOH (De Forcrand, C R 102, 1397. Perhaps identical with Ba(OMe) aq de scribed by Dumas and Peligot (A Ch 58, 17) 1 litre of MeOH dissolves 200 g of BaO The heat of formation of the compound from solid 3BaO and liquid 4MeOH is 62,500 If a considerable quantity of water is added to the solution of BaO in MeOH the hydrate BaO 10aq is precipitated The compound BaO2Ba(OMe), 2aq is readily formed, even if as much as 3 p c water be present in the methyl alcohol, but by evaporating in the cold over H.SO, crystals of Ba(OMe) dag are formed These are sol water and alcohol By passing HCN into a solution of baryta in methyl alcohol there is formed barium cyano methylate Ba(OMe)CN,MeOH This is a crys talline powder, sol water, less sol methyl alcohol It loses at 100° the methyl alcohol of crystallisation

Combinations — CaCl₂VieOH Methyl alcohol dissolves CaCl₂ with great rise of tem perature, and on cooling this compound sepa rates in large six sided tables (Kane, A 19, 168) It is not decomposed at 100°, but water readily liberates the MeOH — LiCl3MeOH — MgCl₂6MeOH (Simon, J pr [2] 20, 377)—SbCl₃MeOH [81°] Slightly yellow crystals (from hot alcohol), decomposes at 130°, giving off MeCl and HCl (W C Williams, C J 30, 463) — CuSO₄2MeOH Minute bluish green crystals, obtained by shaking anhydrous CuSO₄ with methyl alcohol (Forerand, C R 102, 551)

METHYL ALDEHYDE 18 FORMIC ALDEHYDE METHYL - ALIZARIN v DI OX1 METHYL ANTHRAQUINONE

METHYL-ALLANTOIN C, H, N, O, [225°] Formed by oxidising methyl uric acid with cold aqueous KMnO, (Hill, B, 9, 1090) Monoclinic prisms, decomposed by fusion V sol hot water, sl sol alcohol, insol ether Conc HIAq splits it up into urea and methyl hydantom—AgC, H, N, O, prisms, sl sol cold water

METHYL-ÂLLOXAN C₃H₁N₂O₄ te CO NH CO CO Formed by oxidising methyl uric acid with HNO₃ or with KClO₃ and HCl (Hill, B 9, 1092) Formed also by treating theobromine (2 pts) with KClO₄ (9 pts) and HCl (S G 1 06) at 50° (Maly a Andriasch, M 3, 108, of Fischer, A 215, 304) It is converted by alkalis into methyl alloxanic acid, and by boiling HNO₃ into methyl parabanic acid, and by forms di methyl alloxanin KHSO₄ forms a compound B'KHSO₅ aq, which crystallises in large monoclinic prisms

D1 methyl alloxan C_eH_eN₂O₄ a e

CO \ NMe CO \ CO A product of the action of

KClO₄ and HCl on cafferne at 50° It is ex

tracted by ether (E Fischer, A 215, 257, Maly

a Andreasch, M 3, 92) Colourless six sided

tables (containing 2aq), which slowly turn red V sol water, almost insol alcohol, insol in air With FeSO, and Dyes the skin red ammonia it gives a characteristic indigo coloura After drying over H2SO4 it is left as an amorphous powder (containing aq), sol alcohol and ether Di methyl alloxan decomposes at 100° It prevents the ppn of cupric and ferric salts by potash Hydrogen sulphide converts it into amalic acid KHSOs forms the compound C.H.N2O4KHSO, which crystallises in long tablets, S 72 at 20°, almost insol alcohol, insol ether This compound may be crystallised from warm water, and does not give the indigo

colouration with FeSO, and ammonia METHYL ALLOXANIC ACID C,H,N,O Formed by the action of alkalis on methyl-When the product of the action of HNOs on methyl uric acid is neutralised with CaCO₃, and then mixed with alcohol and am monia the salt CaC₃H₄N₂O₃ is ppd (Hill, B 9, 1092) This salt is gelatinous, and when boiled with water it gives off methylamine

METHYL-ALLOXANTIN C,H,N,O, tained by mixing solutions of disluric acid and methyl alloxan (Andreasch, M 3, 431) Ciys tallises from water in minute thin tables (containing 3aq)

s Di methyl alloxantin C10H10N4O8 ve CO < NH CO > C(OH) C(OH) < CO NH CO NH > CO

Formed by passing H S into an aqueous solution of methyl allovan (Maly a Andieasch, M 3, Thin plates (containing 4aq), almost insol alcohol and ether, sl sol cold water Turns 1ed in air Gives a red colouration with ammonia, and a violet colouration with potash or baryta (Andreasch, M 3, 109)

u Di-methyl alloxantin

 $co \stackrel{VMe}{<_{VM}} \stackrel{CO}{<_{VM}} co$

Formed by reducing di methyl alloxan to di methyl dialuric acid, and ppg the aqueous solu tion of this acid with allovan (Andreasch, M 3, Crystallises from hot water in minute four sided pyramids (containing aq), insol alcohol and ether

Tetra methyl alloxantin v AMALIC ACID METHYL ALLYL v BUTYLENE

METHYL-ALLYL ACETO ACETIC ACID • ACFTO ACFTIC ACID

DI METHYL-ALLYL-AMINE Methylo todide C.H.NMe,I From allylamine and MeI (Bono, B 20, Ref 137) When distilled with KOH it yields NMe, and an aldehyde CaHieO (130°-135°)

p METHYL-ALLYL BENZENE C10H12 26 CH₃ C₆H₄ C₃H₅ p Allyl toluene (192°) Formed from cymene by chlorinating and heating the resulting CH₃ C₆H₄ C₃H₆Cl with alcoholic KOH (Errera, G 14, 283, 505) Liquid Combines with bromine KMnO₄ oxidises it to p toluic scid HBrAq (S G 159) at 200° forms a polymeride (C₁₀H₁₂)_x (850°), and this on keeping changes to an amorphous solid, which by distil lation is reconverted into p methyl-allylbenzene

ALCOROL

METHYL - ALLYL - CHLORACETOL v DiCHLORO HEXYLENE

METHYL ALLYL ETHER v METHYL ALLYL

METHYL ALLYL DIKETONE C.H.O. 1 6. CH, CO CO C,H, (c 130°) Acetyl crotonyl Obtained by distilling its mono oxim with dilute H SO₄ (Otte a Von Pechmann, B 22, 2124) Yellow oil with irritating odour Not obtained

Mono oxim CH₃ CO C(NOH) C₃H₃ Nitroso-placetone Methyl nitroso butenyl ketone llulacetone [46°] From allyl aceto acetic acid and nitrous White plates (from ligroin), v sol usual acid menstrua Its solution in NaOHAq is yellow

Di oxim CH, C(NOH) C(NOH) C,H, [135°] Formed from the mono oxim by warming with hydroxylamine Small plates Phenyl hydrazide oxim

CH₃ C(N₂HPh) C(NOH) C₃H₅ [137°] Brownishred needles (from benzene and ligroin)

C4H₂O re (46°) SG 11 METHYL ALLYL OXIDE CH, O C,H, Allyl methyl ether 77 H F p 34,080 H F v 32,050 From allyl bromide and NaOMe (Henry, B 5, 455) bromine it forms CH, O CH2 CHBr CH2Br (185°) ICl gives CH, O C,H, ClI (196°) (Silva, B 8, 1469

METHYL ALLYL PROPYL CARBINOL v

OCTENAL ALCOHOL

METHYL ALLYL SULPHIDE C.H.S t.e CH, SC,H, (c 92°) VD 43 36 Formed by heating lead methyl mercaptide (CH,S),Pb with allyl biomide and ether at 100° (Obermeyer, B 20, 2925

METHYL ALLYL THIO-UREA

[50 5°] CH, NH CS NH C,H, Formed from allylamine and methyl thio carbimide or from methylamine and allyl thio carbimide (O Hecht, White mass B 23, 286)

METHYL AMIDO ACETIC ACID C.H NO. Le CH,NH CH, CO,H Methyl glycocoll Sarcos ine Mol w 89 [210°-215°] Formed by the action of boiling baryta water on creatine or caffeine (Liebig, A 62, 310, Rosengarten a. Stiecker, A 157, 1, Schilling, C C 1884, 811) Formed also by heating chloro acetic ether with aqueous methylamine at 125° (Volhard, A 123, 261)

Properties —Trimetric prisms, v e sol water, sl sol alcohol Has a somewhat sweet taste Heated to 210°-220° the greater part evolves HO giving the anhydride C₆H₁₀N₂O₂, whilst a smaller portion splits up into di methyl amine and CO₂ (Mylius, B 17, 286) Chloride of cyanogen passed into the fused substance gives methyl hydantoin and saicosine anhydride (Traube, B 15, 2110) When taken internally, the greater part passes as such into the urine (Baumann a Mering, B 8, 587, Salkowski, H. 4, 107, Schiffer, H 5, 266) Nitrous and passed into its hot aqueous solution forms a nitrosoderivative CH, N(NO) CH, CO,H, which is a thick liquid, forming the salt $\operatorname{CaA'}_2$ aq crystallis ing in needles (Schultzen, Z 1867, 616) Gives methyl uric acid when heated with urea (Hor baczewski, M 6, 356

Salts—(C.H.NO.),Cu 2aq ultramarıne bluc orystals (E Schmidt, A 217,273) — C.H.NO.HCl needles (from alcohol) —(C.H.NO.),ZnH.Cl, S. (alcohol) 038 V e. sol water (Bulgınsky, J.

1867, 495) — (C₂H₂NO₃) H₂PtCl₂ 2aq monoclinic tables, a b c = 10381 1 6747, $\beta = 75^{\circ}27'$ tables, a b c = 10381 1 6/47, B=75°27' — C₃H₁NO₂HAuCl₄ yellow needles, sl sol cold water—C₄H₂NO₁HNO₃ [c 70°] Very hygroscopic, v sol cold alcohol (Franchimont, R T C 2,839)—(C₃H₁NO₂)₂H₂SO₂ aq four sided tables, v e sol water S (boiling alcohol) 10 Guanidine hydrochloride C₄H₂NO₂HClCH₃N₃ Formed by heating methylamido acetic acid with guanidine hydrochloride (Reumen, R 7, 1151) Tables (from alcohol)

(Baumann, B 7, 1151) Tables (from alcohol)

Anhydride C.H. N.O. 1e

CH, N CH, CO

anhydride Sarcosine OCCH, NCH,

[150°] Formed by the action of cyanogen chloride on melted sarcosine Prepared by heating sarcosine to 210°-220° and distilling the residue (Traube, B 15, 2112, Mylius, B 17, V sol water, al Colourless prisms Weak base cohol, and ether Bitter taste By boiling with water it again gives sarcosine On oxidation with KMnO, it yields s di methyl oxamide

prisms -Salts - B'2H2Cl2PtCl 2aq B'.H.Cl.PtCl.4aq large six sided tables -

B'aHClAuCla 2aq prisms

Sarcosine-uric acid C₈H₂O₄N₃ Obtained by heating a mixture of sarcosine (3 pts) and uric acid (2 pts) at 210°, a good yield is obtained

Properties - Colourless prismatic crystals (containing 2aq) Sol hot water It shows the murexide reaction It slowly reduces alkaline solutions of copper It has weak acid and basic properties, dissolving in aqueous acids and alkalis By fusion with KOH at 110° it is resolved into uric acid and sarcosine Heated with bromine water it is converted into bromo sarcosinemesouric acid C₈H₇N₄O₅Br

Salts -The acetate forms microscopic crystals, sl sol hot acetic acid, insol cold HOAc, v sol water The formate is very analogous to the acetate The ammonium salt is crystalline -A"Ag, insol white amorphous pp (My lius, B 17, 518)

Bromo-sarcosine mesouric acid C.H.N.O.Br Formed by digesting a warm aqueous solution of sarcosine uric acid with bromine, which gives a nearly theoretical yield (Mylius, B 17, 521) Heavy colourless tables Sl sol water By H2S it is reduced to sarcosine mesouric acid It is readily decomposed by alkalis, but is stable towards acids

Sarcosine-mesouric acid CaHaOaN. Obtained by reducing a hot aqueous solution of bromo sarcosine mesouric acid with H.S (Mylius, B 17, 524) Trimetric tables or needles V sol water, insol alcohol It is a strong acid, but also possesses weak basic properties By bromine water it is reconverted into the bromo derivative, similarly chlorine water gives the chloroderivative It is very oxidisable, reducing AuCl, alkaline, copper solution, KMnO4, &c, very

Salts-The acetate forms an unstable crystalline pp, sl sol acetic acid -A"HNH, fine needles, v sol water -A"Ag, white amor

phous pp

Tri-methyl-amido acetic acid internal anhydride v BETAINE.

DI-METHYL-AMIDO ACETIC ORTHAUDE Methylo-hydroxide C,H,,NO, se HYDE CH (NMe₃OH) ČH(OH)₂. Muscarine Occurs, together with neurine, in the fly agaric (Schmie deberg a Koppe, J 1870, 875) Formed from neurine by oxidation with conc HNO, (Schmie deberg a Harnack, J 1876, 804) Deliquescent crystalline mass, sol alcohol Alkaline in reaction Active narcotic poison Separated from neurine by placing the mixed hydrochlorides on filter paper, when the muscarine salt deli quesces and is absorbed by the paper (Harnack, J 1876, 803) —B'(C₅H₁₁NO₂Cl)₂PtCl, 2aa --C₅H₁₁NO₂AuCl, Dr-ethyl derevative of the methylo

hydroxide C.H., NO, ie CH, (NMe, OH) CH(OEt), Hydroxide of tri When chloro acetal methyl - amido - acetal CH2Cl CH(OEt)2 is treated with tri-methyl amine there is formed CH, (NMe, Cl) CH(OEt), and C₃H₁₂NOCl, which is probably CH₂(NMe₃Cl) CHO The two salts are separated by fractional ppn by platinic chloride -(C,H22NO2Cl)2PtCl, orange crystals, sl sol cold water — C. H. NO, AuCl, lemon yellow needles

Di methyl amido acetic aldehyde Methylo hydroxide C₅H₁₈NO, ie CH₂(NMe₃OH) CHO Formed by saponifying CH₂(NMe₂OH) CH(OEt), with baryta (Berlinerblau, B 17, 1142) hydrochloride C₅H₁₂NOCl is also formed as above Gives the aldehyde reactions -Platinochloride (C₃H₁₂NOCl), PtCl, octahedra (from dilute

alcohol)

DI METHYL-AMIDO-ACETONE Methylochloride C₀H₁₄NOCl ie CH₂CO CH₂NMe₂Cl Caprine chloride Formed by the action of dry NMe, upon chloro acetone in the cold (Niemitovitch, M 7, 241) Very deliquescent shining needles, sol alcohol Gives the alkaloidal re actions Acts physiologically like curare — C₆H₁₄NOClAuCl, [139°]

DI-METHYL-AMIDO-ACETOPHENONE C₆H₄(NMe₂) CO CH₃ [59°] Formed by methylation of p amido acetophenone (Klingel, B 18, 2694) Yellowish plates (from hot water) ∇ sol alcohol, ether, and hot water

o DIMETHYL AMIDO ANISOL o Dr. METHYL-AMIDO PHENOL methyl ether

METHYL AMIDO-AZO- COMPOUNDS 1 Azo-

COMPOUNDS METHYL AMIDO BENZAMIDE v Amide of METHYL AMIDO BENZOIC ACID

METHYL-AMIDO BENZENE ANILINE and TOLUIDINE

Di-methyl-amido-benzene v Xilidine. METHYL TOLUIDINE, and DI METHYL-ANILINE

Tri-methyl amido benzene v Mesiding and **♥** CUMIDINE

Tetra - methyl amido - benzene v TETRA METHYL PHENYL AMINE

Tetra methyl di amido benzene 😻 TETRA METHYL-PHENYLENE DIAMINE

Di-methyl-tra-amido-benzene

C₆H_s(NMe₂)(NH₂), [1 8 4] [44°] (298°) Needles. Readily turned blue in the air Prepared by reduction of dinitro dimethyl aniline $[\hat{s7}^{\circ}]$ Formed also by reduction of nitro-p dimethyl amidophenyl oxamic ether

Acetyl derivative

C₆H₃(NMe₂)(NH₂)(NHAc) [153°] Prisms (containing aq) (Wurster a Sendtner, B 12, 1805).

u-Tri-methyl-tri-amido-benzene $C_0H_2(NMe_2)(NH_2)(NHMe) [1 x 4] [90°] (294°)$ Prepared by reduction of the nitrosamine de rived from nitro trimethyl p-phenylene diamine (Wurster a Schobig, B 12, 1812) White needles Sol water Gives a blue colouration with HNO.

Diacetyl derivative [184°] Leaflets METHYL-AMIDO-BENZENE-AZO- COM-POUNDS v Azo- compounds and Dis Azo- com-

DI - METHYL - AMIDO - BENZENE PHOS PHINIC ACID NMe2 C6H4 P(OH)2 [162] Formed by decomposing its chloride with water (Schenk a Michaelis, B 21, 1498) needles, v sol hot water and alcohol On boiling its aqueous solution it is split up into di-methyl aniline and phosphorous acid When heated alone it gives phosphorus, PH2, and di methyl aniline

Salt -NaHA" 2aq large crystals (from alcohol)

(250° at Chloride NMe2 C.H. PCl2 [66°] 120 mm) Formed by the action of PCl, (100 g) on di methyl aniline (70 g) in presence of AlCl, (20 g) The mixture is boiled for eight hours with inverted condenser, and the product ex tracted with petroleum ether and distilled in vacuo. Thin plates, v sol benzene, m sol ether, sl sol petroleum ether. Converted by the action of chloro benzene and sodium into

DI-METHYL AMIDO BENZENE PHOS [133°] PHONIC ACID NMe C₆H₄ PO(OH) Formed by oxidising NMe.C.H. P(OH), with HgCl₂ (Schenk a Michaelis, B 21, 1500)

Crystals, v e sol water and alcohol

dı methyl amıdo trı phenyl phosphine

METHYL AMIDO BENZENE SULPHONIC ACID C, H, NSO, te NHMe C, H, SO, H Formed, together with methane disulphonic acid, by heating the acetyl derivative of methyl aniline with H₂SO₄ at 145° (Smyth, B 7, 1240) Crystals, which decompose at 182° without previous fusion -BaA'aq crystalline powder

Methyl-amido-benzene sulphonic acid NHMe C.H. SO3H Formed by heating methylaniline ethyl sulphate at 210° (Mundelius B 7, 1350) Plates (containing aq), insol alcohol and ether — BaA'₂3'₁aq small prisms
CaA' 4aq —PbA'₂8aq
D1-methyl-amido-benzene p-sulphonic acid small prisms -

NMe C.H. SO.H [150°] (S), [257°] (M a G)

Formation -1 By heating di methyl aniline with rather more than the equivalent quantity of sulphuric acid at 185° (Smyth, B 6, 344, 7, 1237, Armstrong, B 6, 663, Vignon, C R 107, 263) -2 From di methyl aniline and ClSO, Et (Wenghoffer, J pr [2] 16, 448) —3 From bromodi methyl-aniline and H SO, at 180° (Michler a. Walder, B 14,2177) -4 From di methyl aniline and SOCl, followed by water (Michaelis a God-chaux, B 23, 555)

Properties -8 sided prisms (containing aq).

Decomposes at 230°

efflorescent aqueous NaOH, insol water (M a G.)

Chlorede C.H. (NMe.)SO.Cl.

Ethyl ether EtA' [85°] Formed from alcohol and the chloride

Di-methyl-amido-benzene p-sulphonic acid Anhydride of the methylo hydroxide $C_0H_{13}NSO_3$ re $C_0H_4 < \frac{NMe_3}{SO_2} > 0$ Formed allowing a mixture of amido benzene p-sulphonic acid, MeI, cone KOHAq, and MeOH to stand for some time in the cold (Griess, B 12, 2116) Four sided plates, v sol cold water, almost insol alcohol, insol ether Decomposes before fusion Ppd as periodide by a solution of rodine in HIAq (SO3H.C4H4 NMe3Cl) PtCl4 8aq orange tables, v e sol cold water

METHYL-o-AMIDO-BENZOIC ACID

Amide NHMe C.H. CONH2. [160°] Formed by heating o amido benzamide with MeI at 100° (Weddige, J pr [2] 36, 152) Plates, v sol hot alcohol, sol water In dilute solutions it shows blue fluorescence

Acetyl derivative NHMe C₈H, CO NHAc [155°] Long needles, v sol hot alcohol, sl sol benzene and ether When heated above 155° it forms the anhydro derivative $C_{\bullet}H_{\bullet} < \stackrel{CO \ N}{\sim} NMe > CMe [199^{\circ}]$ which is

an oxy di methyl quinazoline

Nitroso derivative of the amide NO NMe C₆H₄ CO NH₂ [149°] Pale yellow prisms (from hot alcohol) (Finger, J pr [2] 37,

Methyl-m-amido-benzoic acid C₈H₂NO₂ a.e NHMe C.H. CO.H Formed by boiling (a)-benzcreatin NH C(NH) NMe C.H. CO.H with baryta water (Griess, B 8, 325) Nodular groups of plates, v sol hot water Nitrous acid ppts a nitroso- derivative Salt -C,H,NO,HCl sixsided plates

Di methyl-m-amido-benzoic acid C.H., NO. s.e NMe₂C₆H₄CO₂H [151°] Obtained by saponifying its methyl ether Needles, sl sol hot

Methyl ether NMe, C,H, CO,Me uncor) Obtained by fusing the isomeric anhydride of the methylo hydroxide (v. infra) (Griess, B 6, 587) Heavy yellowish oil, sol acids -C,H10MeNO2H2SO, very small prisms, sl sol dilute sulphuric acid, v sol water -(C.H. MeNO).H.PtCl, spindle shaped laminæ, ▼ sl sol cold water

Anhydride of the methylo-hydroxide C10H13NO, 16 C6H4< NMe3>0 Formed by allowing a mixture of m amido benzoic acid with MeOH (1 mol.), aqueous KOH (3 mols), and MeI (3 mols) to stand in the cold, the product, after freeing from MeOH by distillation, being saturated with HI, whereupon the rodide NMe, I CoH, CO2H is ppd This rodide is then boiled with water and lead hydroxide (Griess) Small deliquescent needles (contain ing aq), which give up their water of crystallisa-tion at 105° V e sol cold alcohol, insol ether Tastes bitter and is neutral in reaction Forms (NMe,Cl C,H, CO,H),PtCl, 4aq crystallising in large prisms, sl sol hot water_____

Methylo rodide NMe, I CoH, CO2H Formed Small short pusms (containing aq), as above al sol cold water

NMe,Cl C,H, CO,H. Methylo-chloride

D1-methyl-p-amido-benzoic acid NMe₂ C₆H₄ CO₂H [235°] Forme Formed by boiling its chloride with water Prepared by boiling for three hours a mixture of p amido benzoic acid (1 mol), MeI (2 mols), and aqueous KOH (3 mols) dissolved in methyl alcohol (Michler, B 9, 400) Obtained also by heating tetra methyldi amido benzophenone with soda lime at 340°, extracting the product with hot water, and ppg by acetic acid (E. Bischoff, B. 22, 341) Short needles (from alcohol), sol aqueous KOH and HClAq, insol dilute acetic acid Nitrous acid forms NMe C₆H₃(NO) CO₂H [224°] The Ca salt forms yellowish plates

Methyl ether NMe_CeH, CO2Me [102°] Silvery plates (from alcohol), v sol benzene, ether, and chloroform, m sol dilute alcohol Nitrous acid forms NMe₂ C₆H₃(NO) CO Me 6 aq

[101°]

Chloride NMe, C,H, COCl Obtained by heating di methyl aniline with COCl₂ at 50° in a

sealed tube (Michler) Crystalline
Nitrile NMe C₈H₄ CN From di methyl p phenylene diamine by Sandmeyer's reaction

(Ahrens, B 20, 2958)

Anhydride of the methylo hydroxide $C_{10}H_{13}NO_2$ i.e $C_8H_4 < \frac{NMe_3}{CO} > O$ [c 255°] When p amido benzoic acid is mixed with MeI, KOH, and methyl alcohol, there is formed, even in the cold, di methyl p amido benzoic acid and the iodide NMe₃I C₀H₄CO H which crystallises in short yellow plates [233°] (Michael a Wing, Am 7, 195) The corresponding anhydrida srystallises from alcohol in colourless plates (containing aq), v sol water It loses its water of crystallisation at 100° The periodide forms long dark prisms [200°] (NMe₂Cl C₆H₄ CO₂H)₂PtCl₄ The platinochloride torms large prisms

Tetra-methyl-di-amido-benzoic acid Da.

methylo di-hydroxide (HO NMe₃)₂C₆H₃CO₂H [1 3 5] The iodide (INMe₃)₂C₆H₃ CO₂H aq is formed when di amidobenzoic acid (1 pt) is mixed with MeI (6 pts), methyl alcohol (10 pts), and twice as much of a concentrated solution of KOH as is required to neutralise the acid The mixture should stand for some time, being kept alkaline by further additions of potash The alcohol is then dis tilled off, and the iodide ppd by HIAq (Griess, This iodide crystallises from hot B 7, 39) water in six sided tables or plates, v sol hot With moist Ag₂O it yields a caustic alkaline liquid which, on evaporation, leaves the hydroxide as a hygroscopic mass of soft white plates It rapidly absorbs CO, and ppts metallic oxides from their salts. The corresponding chloride (NMe3Cl)2C6H3CO2H4aq, obtained by neutralising the hydroxide by HCl, crystallises in small six sided plates, v sol water, sl sol hot alcohol The periodide forms brownish yellow needles The carronate

CO NMe₃ C₈H₂ CO₂H 3aq, obtained from the iodide and Ag₂CO₂, crystallises from water in very small soluble plates, having an alkaline reaction. The platinochloride (CiNMe₃)₂C₆H₁ CO₂HPtCl₁aq is a pp composed

Monoclinic crystals, a b c=1 939 1 0 876, of very small pale yellow plates, usually grouped $\beta=88^\circ$ 49' (Zingel, Z K 10, 414) in stars

Derivative v CHLORO METHYL AMIDO BEN ZOIS ACID

DI - METHYL-p-AMIDO - BENZOIC ALDE-HYDE, C₂H₁₁NO i e NMe C₄H₄CHO [73°] Formed, together with CHCl₃, by heating NMe₂ C₈H₄ CH(OH) CCl₃ with alcoholic KOH (Bossneck, B 18, 1520, 19, 366) With di methyl aniline and hydrochloric acid it forms

(NMe₂ C₆H₄),CH Oxim NMe₂ C₆H₄ CH NOH [144°] Yellow ish brown plates (Knöfler a Bossneck, B 20,

Phenyl hydrazide NMe C.H.CH N.HPh [148°] Needles (from alcohol)

DÍMETHYL AMIDO BENZOPHENONE

C,H, CO C,H, NMe Benzodimethylaniline Benzoyl di methyl aniline Benzoyl phenyl di methyl amine [90°] Formed by heating the methylo iodide to 181° Formed also by heat ing malachite green (NMe C_sH₄)₂C(OH) C_sH₄ with conc HClAq at 180° Colourless plates (from alcohol) Insol water, sl sol cold alcohol, v e sol hot alcohol or ether It is a feeble base, its solution in concentrated acids being ppd by water

C,H, CO C,H, NMe,I Methylo rodide Large tables, sl sol cold water Formed by heating p amido benzophenone with MeI at 100° It decomposes at 181° (Doebner a Weiss,

B 14, 1836, A 210, 270, 217, 257)

Di methyl-amido-benzophenone C.H. CO C.H. NMe. [39°] (330°-340°) Ob tained by heating benzoic acid with di methyl aniline and P2Os at 185° (O Fischer, A 200, Needles (from ligroin) Forms unstable With nitrous acid it yields the oily salts nitroso derivative C₆H₅ CO C₆H₃(NO)NMe₂ (E Bischoff, B 22, 340)

D1-methyl-d1-p-amido-benzophenone

benzoyl derivative C., H., NO, ie (NMeBz C.H., 200 [102°] Formed by heating tetra methyl di amido benzophenone with BzCl at 190° (Nathansohn a Muller, B 22, 1877) Small light brown plates, sl sol cold, v sol hot, alcohol, sl sol benzene, almost msol water and ether Acids and alkalis at 100° do not saponify it

Tri-methyl-di-amido-benzophenone

NHMe C₆H₄ CO C₆H₄ NMe₂ [156°] Formed, together with di methyl aniline, by boiling penta methyl-tri-amido tri phenyl-carbinol HClAq (Wichelhaus, B 19, 109) Nodular groups of needles (from alcohol)

Tetra-methyl-di-amido-benzophenone $NMe_2 C_6H_4 CO C_6H_4 NMe_2 [172°]$ (above 360°)

(Græbe, B 20, 3262)

Formation -1 By passing COCl, into di methyl anılıne (Michlei, B 9, 716, 1900) -2 By boiling hexa methyl tri amido tri phenol carbi nol with HClAq (Wichelhaus, B 19, 109) — 3 From CCl₂ SO₂Cl and di methyl amline (Mich-

ler a Moro, B 12, 1168)

Preparation — By boiling auramine with aqueous HCl till decolourised, and ppg with

NH,

Properties - White plates (from dilute alcohol), insol water, m sol alcohol, v e sol warm benzene, v sl sol ether

Reactions -1 Heating with ZnCl, and

NH₄Cl at 160° produces auramine (Fehrmann, B 20, 2844) —2 Boiling HNO₅ (S G 148) gives insoluble yellow crystals of tetra nitro di methyldi nitramido benzophenone and tri nitro phenylmethyl nitramine [127°], soluble in alcohol (Romburgh, R T C 6, 867)—3 Excess of bromine added to a solution of the base in glacial acetic acid gives the tetra-bromo derivative (C_eH₂B₁,NMe₂),CO [172°] which crystallises in slender yellow needles from alcohol (Nathansohn a Muller, B 22, 1883) -4 Heating with amline hydrochloride yields phenyl auramine -5 Combines with tri nitro benzens (2 mols) forming a compound which crystallises in long reddish violet needles [c 100°] With half the quantity of tri nitro benzene (1 mol) it forms small deep violet plates [123°] 6 Combines with m di-nitro benzene (2 mols) forming a red crystalline compound —7 Nitrous acid in the cold forms the nitroso- derivative NMe C₆H₄ CO C₆H₂(NOH) NMe [159°] crystal lising from alcohol in golden plates This sub stance is a weak base, its solution in HClAq being ppd by water It gives Liebermann's reaction Stannous chloride reduces it to the original tetra methyl di amido benzophenone The nitroso derivative forms the following salts B"H2Cl2 Obtained by passing HCl into a solution of the nitroso ketone in benzene -B"C, H (NO₂), OH [152°] Orange needles (from alcohol) The nitroso ketone gives also a phenyl hydrazide $C_2H_2N_3O_3$ [148°] (L. Bischoff, B. 21, 2452, 22, 337) —8. In presence of dehydrating agents, such as PCl, or AlCl, it condenses with secondary and tertiary bases. Thus with di methyl aniline it yields 'crystal violet' C(OH)(C₆H₄NMe)

Salts -B"H Cl, small radially grouped prisms (from alcohol) Decomposed by water, with separation of the base (Fehrmann, B 20, 2844) -B"H PtCl_e yellow granules, insol water, v sl sol alcohol -Picrate B"C,H (NO2),OH [157°] Small, purple, 1ad1 ally grouped, prisms (from alcohol), insol cold,

v sl sol hot, water, m sol alcohol

Di methyl di rodide B"Me,L₂ [105°]

Light yellow plates (from alcohol), sl sol cold, v sol hot, water and alcohol Split up at 150° into MeI and the base (Nathansohn a Muller, B 22, 1876)

Dr methylo-dr-hydroxide B"Me2(OH) From the preceding and moist Ag O yellow plates (from alcohol), quickly becoming

dark and resinous (N a M)

Oxim HON C(C_cH, NMe₂)₂ [233°], colourless crystals (Munchmeyer, B 19, 1852, 20,

Phenyl-hydraside C2H2N, 16 (NMe₂,C₄H₄),C N HPh [175°] Needles (from benzene-alcohol), m sol warm alcohol, v sol ether Coloured green by acid oxidising agents (Ziegler, B 20, 1111) Conc H₂SO, gives a red colouration

Imide (NMerC.H.)2C NH Auramine base [136°] Formed by heating tetra-methyl-di-amido benzophenone with NH₄Cl and ZnCl₂ at 150° to 160° Formed also by treating a solution of tetra methyl-di-amido benzophenone in CS, with PCl, and subsequently adding ammonia (Caro a. Kern) (cf AURAMINE in THORPE'S DIC-TIONARY OF APPLIED CHEMISTRY). Lemon-yellow

plates, insol water and ether, m sol alcohol Dilute HClAq readily converts it, even in the cold, into tetra methyl di amido benzophenone

Reactions -1 Sodium amalgam reduces it (in alcoholic solution) to leucauramine $C_0H_1NMe_2$), CH NH₂ [135°] This substance forms colourless crystals which when treated with HOAc yield an intense blue solution (Græbe, B 20, 3265) —2 H₂S in alcoholic solu tion at 60° forms tetra methyl di amido thio benzophenone [164°] —3 CS₂ also forms (NMe₂C₈H₄)₂CS together with thiocyanic acid

(Fehrmann, B 20, 2847) Salts—B'HCl aq Auramine Yellow six sided tables (from water at 70°) After expulsion of the water it melts (G) or decomposes (F) at 267° M sol cold water, m sol alcohol Boiling water converts it into tetra methyl di-amido benzophenone Dyes wool and silk greenish yellow Cotton prepared with tannin is also dyed yellow by auramine —B'₂H₂PtCl₆ granules, insol water, sl sol alcohol —B'HI [268°] Minute columns -B'HSCy aq [200°-210°] -B'H,C2O4 [194°] Orange needles, sl sol water, m sol warm alcohol—B'C₆H (NO₂)₃OH [230°-236°] Plates, msol cold, v sl sol hot, water, m sol hot alcohol

Phenyl imide (NMe₂ C₈H₄)₂C NPh Formed by heating the hydrochloride of the imide (auramine) with aniline at 180° (F), Small greyish-yellow radially grouped needles (from alcohol), decomposing at 80° Insol water and ether —B'HCl reddish crystalline mass, sol water and alcohol Its aqueous solution gradually decomposes, yielding aniline and tetra methyl di-amido benzophenone -B',H2PtCl, -B'C₆H (NO₂),OH

p Tolyl imide (NMe, C, H,)2C NC, H,Me Resembles the phenyl imide -B'.H.PtCl. Ethylene-dr-amide C19H28N4 1.e

NH CH2 $(NMe_2 C_6H_4)_2C <$ Formed by heating NH CH,

auramine (hydrochloride) with ethylene diamine at 100°-110° (Fehrmann, B 20, 2855) Yellowish plates (from alcohol), insol water, m sol warm alcohol On treatment with HOAc or dilute HClAq it decomposes into ethylene diamine and (NMe2 C8H4)2CO In alcoholic solution it is de composed by H.S into ethylene diamine and (NMe₂ C₆H₄)₂CS -B"H₂Cl₂ yellow needles -B"H₂PtCl_s amorphous flakes, insol water and ether, v sol warm alcohol—B"2C_gH₂(NO₂)₃OH flakes, v sl sol water, v sol alcohol.

Tolylene di amide (NMe, CeH4), C<NH>CeH2Me Formed by heating the hydrochloride of the imide (auramine) with (1, 2, 4) tolylene diamine at 160°, and treating the product with ammonia brown scales In dilute acetic acid solution it dyes cotton, mordanted with tannin, reddishbrown Dilute HClAq regenerates the original ketone —B"H.PtCl, —B"2C.H.(NO.), OH
Tewa-methyl-tri-amido-bensophenone

C₁,H₂₁N₂O se NMe₂,C₂H₄ CO C₂H₃(NH₂)(NMe₂) [82°] Obtained by reducing nitro-tetra methyldi amido benzophenone (Nathansohn a Müller, B 22, 1884) Amorphous yellow powder, v sol hot, sl sol cold, alcohol and benzene, insol ether —B'C₂H₂(NO₂)₂OH minute plates, v sol. creatinine

hot alcohol, insoluble in benzene and ether -B'2H.PtCl, light red crystalline pp, v sol warm alcohol, sl sol benzene, insol water and

METHYL-g-AMIDO-n-BUTYRIC ACID C₅H₁₁NO₂ is CH₂CH₂CH(NHMe) UU₂H.
Formed by heating a bromo-butyric acid with a concentrated solution of methylamine in sealed tubes at 100°. The product is boiled with baryta to expel NH2Me, the Ba exactly ppd by H2SO4, and the HBr by Ag₂CO₃ (Duvillier, A Ch [5] 20, 188, C R 88, 425) Glistening leaflets (from alcohol), subliming above 120° without V e sol water, m sol hot alcohol, insol Has a sweet taste Feebly acid in re ether action By the prolonged action (several months) of cyanamide (1 mol) in concentrated and slightly ammoniacal solution it is converted into but yro-CH, CH, CH CO NH N(CH,) C NH

which crystallises from alcohol in slender silky needles composed of small rectangular plates

CDuvillier, C R 95, 456, Bl [2] 39, 539)

Salts -HA'HCl [150°] Badly defined crystals, sol alcohol, insol ether Gives off HCl on fusion -H₂A'₂H₂PtCl₅ orange red crystals, v sol water and alcohol, insol ether -H₂A'₂H₂PtCl₆5aq Formed at 0'—HA'HAuCl₄aq transparent yellow prisms, sol water, alcohol, and ether - The nitrate and sulphate crystallise with difficulty in long needles - CuA', 2aq light-blue prisms, sol alcohol

Di methyl a amido-butyric acid Anhudride of the methylo-hydroxide C,H, NO.

CH, CH, CH—CO Tri - methyl - a amido-(CH₂)₂N — O

butyro - betaine Prepared by the action of bromo butyric ether on an excess of tri methylamine in alcoholic solution (Duvillier, C R 104, 1520) Large transparent crystals, containing aq, which they lose at 120°, becoming opaque, v sol. water and alcohol, insol ether Has a bitter taste - B'HCl Uncrystallisable B'2H2PtCl8 orange prisms, sl sol alcohol The aurochloride forms yellowish white

METHYL AMIDO-CAPROIC ACID v METHYL-AMIDO HEXOIC ACID

METHYL - AMIDO - CHLORO- v CHLORO-METHYL-AMIDO

METHYL - AMIDO - CYANURIC ACID v CYANIC ACID.

METHYL-AMIDO - ETHANE SULPHONIC ACID C₂H₄NSO₂ r.e. CH₂NH.CH₂CH₂SO₃H Methyl-taurine [242°].

Formation — From methyl-ethylene-\psi thiourea and bromine-water (Gabriel, B 22, 1148)

Preparation — Silver chloro - ethane sul-phonate is heated with 8 times its weight of a solution of methylamine, saturated at 0°, for 5 hours at 120° The product is boiled with baryta to expel excess of methylamine, freed from excess of baryta by H.SO., and evaporated to crystallisation The crystals are washed with alcohol and recrystallised from water The yield 18 25 p.e (E. Dittrich, J. pr. [2] 18, 68)
Properties—Transparent triclinic crystals

Sol water, insol alcohol and ether Its aqueous solution is acid to litmus Crystallises un-

altered from strong HCl Does not form salts with acids and alkalis

Reactions —1 N₂O₃ forms isethionic acid, (HO)CH₂ CH₂ SO₃H —2 With cyanamide it combines to methyl taurocyamine or methyl guanidoethane sulphonic acid

Di methyl amido ethane sulphonic acid

NMe₂.CH₂ CH₂ SO₃H Formed by heating di methylamine β chloro ethane sulphonate (20 g) with aqueous (33 pc) dimethylamine (5 g) at 160° for 10 hours (James, J pr [2] 31, 416, C J 47, 370) Large tables (from water), v e sol water, insol ether Decomposes at 270°-280° without fusion Does not combine with HCl

Anhydride of the methylo hydroxide $CH_2 NMe_3 > O$ Formed by heating β chloro-CH_SO, ethane sulphonic acid with aqueous tri methyl amine Slender prisms (from water), v sol water, insol alcohol and ether Neutral in re action Tastes sweet Not decomposed at 300° Not acted upon by cyanamide Baiyta gives NMe_3 and isethionic acid (James, C J 49, 489)

DI-METHYL-AMIDO-ETHYL ALCOHOL v

DI METHYL-OXYETHYL AMINE

DI METHYL AMIDO ETHYL BENZENE DI METHYL AMIDO PHENYL ETHANE

METHYL-AMIDO-ETHYL KETONE

CH, CO CH(NH2) CH, Perhaps formed by re ducing methyl nitroso ethyl ketone, but if so it quickly changes to s-tetra METHYL PARAZINE

METHYL-AMIDO-FORMIC ACID v MFTHYL-CARBAMIC ACID METHYL-a-AMIDO n HEXOIC ACID

C,H,NO, 26 $\mathbf{CH_3}\,\mathbf{CH_2}\,\mathbf{CH_2}\,\mathbf{CH_2}\,\mathbf{CH}(\mathbf{NHMe})\,\mathbf{CO_2H}$ amido caproic acid 8 10 2 at 11° Formed by heating a-bromo-hexoic acid (1 mol) with aqueous methylamine (2 or 3 mols) at 100° for several hours (Duvillier, C R 90, 822, A Ch [5] 29, 165) Silky needles (from water) or pearly plates (from alcohol) Sl sol cold alcohol, insol Neutral in reaction Volatilises above ether 100° Does not reduce silver or mercurous nıtrate Gives with ferric chloride an intense red colouration and a yellowish brown pp An equivalent quantity of cyanamide in cold concentrated solution containing a few drops of

NH, forms in a few weeks crystals of 'hexoic creatinine' C,H, CH CO NH NMe C ŇH

cold water, v sol alcohol (Duvillier, C R 96, 1583, Bl [2] 40, 307) -HA'HCl transparent plates, v sol water and alcohol, insol ether -H₂A'₂H₁PtCl₈ orange crystals, v e sol water, v sol alcohol, v sl sol ether—The aurochloride forms golden needles, the sulphate forms very indistinct crystals -CuA' 22aq blue scales, S 1

Di methyl amido-hexoic acid Methylohydroxide HO NMe, C.H., CO.H. Formed by heating leucine (1 mol) derived from casein with aqueous KOH (3 mols), and MeI (3 mols) The resulting INMe, C₂H₁₆ CO₂K, which crystallises from alcohol in needles, being decomposed by moist Ag₂O (Korner a Menozzi, G 13, 353) Strongly alkaline Decomposes at 120°-130° into trimethylamine, an acid, CsH10O2, and oxyhexore and Forms the platinoch oride

(ClNMe, C_aH_{10} CO₂H). PtCl, aq, a urochloride Cl, AuNMe, C_aH_{10} CO₂H [163°], and periodide The periodide forms lustrous green crystals, decomposed by H₂S, yielding INMe, C₃H₁₀ CO₂H [191°], crystallising in small prisms

DI-METHYL-AMIDO-HYDROQUINONE C₆H₃(NMe₂)(OH)₂[241] Di mathyl derivative C₆H₄(NMe₂)(OMe)

Methylo rodide B'MeI [202°] Formed by heating the di methyl derivative of amido hydroquinone with methyl iodide (Bæssler, B 17, 2122) White needles, v sol water, sl sol absolute alcohol, nearly insol benzene, chloro form, and ligroine

Methylo hydroxids B'MeOH

needles

Methylo chloride B'MeCl white easily soluble needles [172°] -(B'MeCl)2PtCl, yellow crystalline pp

TRI METHYL-AMIDO IMIDO IMIDO DI-PHENYL SULPHIDE Methylo chloride C16H16N2SCl 2 e N C2H2(NMe) S Methylene

NMe₂Cl blue Chloride of tetra methyl thionine

Formation -1 By the action of H.S on an acid solution of nitroso di methyl aniline and oxidation of the resulting leuco methylene blue In this reaction di methyl p phenylene diamine is an intermediate product (Caro, E P 1877, 3751, Koch, B 12, 593, Bernthsen, A 230, 137) - 2 By dissolving nitroso di methyl aniline in H.SO4 (S G 14), treating with sulphide of zinc, and oxidising the resulting leuco methyleneblue (Oehler, G P 1882, 24,125, Muhlhauser, D P J 262, 371) -3 By exidation of di methylp phenylene diamine in presence of Na2S2O3, and further oxidation of the resulting C_nH₃(NMe₂)(NH₂)S SO₃H by chromic acid (Bernthsen) —4 By reducing the compound C_sH₃(NMe₂)(NH₂)S SO₃H to C_sH₃(NMe₂)(NH₂)S H and oxidising a mixture of this mercaptan with di methyl aniline with HCl and K2Cr O,, the 'soluble green' resulting C₁₆H₁₉N₂S $N < C_6H_4(NMe_2) > S$ slowly changing in aqueous

solution to methylene blue (Bernthsen, A 251,

Properties -Minute dark blue laminæ (con taining 3aq), v sol water and alcohol mordanted cotton blue Its aqueous solution is blue and not affected by HCl or ammonia NaOH gives a violet colour and, when added in large quantity, a dirty violet pp H.SO, gives a yellowish green solution, becoming blue on dilution. The aqueous solution is decolourised by H₂S or Na₂S₂O₃, the colour is restored even by feeble oxidising agents Sodium hyposulphite Na, S,O, reduces it to the leuco base Fuming HClAq at 260° decomposes it, giving off H2S Boiling dilute HNO. oxidises it, forming H.80. Boiling aqueous KOH forms 'thionol,' the anhydride of di-oxy-

mido-di phenyl sulphide NC₀H₂(OH)>8

Salt -- (C1.H1.N.SCI), ZnCl, aq.

Formed by treating methylene blue with moist Ag.O Amorphous, dark blue mass, v e sol. water and alcohol, insol ether

Methylo rodide C₁₆H₁₈N₂SI bronzy dles (from hot water) The di chloro derineedles (from hot water) vative of this iodide $C_{1s}H_{1s}Cl_sN_sSI$ is formed by successive treatment of di chloro di methyl p phenylene diamine C_sH $Cl_s(NMe_s)(NH_s)$ with H₂S, FeCl₃, and KI (Mohlau, B 19, 2012)

TRI METHYL-AMIDO IMIDO-IMIDO-DI-PHENYL-SULPHONE Methylo-rodide $C_{16}H_{18}N_3SO_2I$ i.e. $N < C_6H_3(NMe_2) > SO_2$. Methy l-NMe₂I

Formed, together with methylene ene azure violet, by boiling methylene blue with Ag2O and a large quantity of water (Bernthsen, A 230, Slender needles with green lustre, sol water, forming a violet solution from which it is ppd by KI Alkalis destroy the colour of the solution The corresponding C₁₆H₁₈N₂SO₂Cl crystallises in needles, v e sol water It dyes silk like methylene blue

TETRA METHYL-DI AMIDO-IMIDO DI-PHENYL METHANE v Imide of Tetra-METHYL-DI AMIDO-BENZOPHENONE

METHYL-DI-AMIDO IMIDO DI-PHENYL SULPHIDE $C_{13}H_{13}N_2S$ s.e $NMe < C_0H_2(NH_2) > S$

Methyl di amido thio diphenylamine Formed by reduction of di nitro methyl imido-di phenyl sulphide with tin and HCl (Bernthsen, A 230, 130) Insol water, sol ether The dilute solu tion of its hydrochloride is coloured blue by FeCl, —B"H,Cl. Needles, v sol water, almost insol HClAq

Tetra methyl-di-amido-imido-di phenyl sul- $NH < \stackrel{C_0H_3(NMe_2)}{C_0H_2(NMe_2)} > S$ phide C, H, N,S .c Leuco methylene blue methylene blue with Formed by treating hyposulphite sodium Na₂S₂O₄ (Bernthsen, A 230, 147) Needles (from alcohol), sl sol water, m sol cold alcohol Gives an acetyl derivative, v sol alcohol, ether and benzene With MeI it forms NMe C.H.(NMe,I)>8 crystallising in plates, v sl sol water and alcohol, insol ether Oxidised by air to methylene blue—B'H₂ZnCl₄ prisms Di-methyl amido imido phenyl disulphide

Methylo chlorede C.H.N.S.Clas C,H, NMe₂Cl $\langle | N-S \rangle$ S Methylene red A by pro-

duct in the manufacture of methylene-blue from dı methyl p phenylene diamine and H₂S followed by FeCl₂ (Bernthsen, A 230, 165, 251, 22, Koch, B 12, 594) Small green glittering prisms (from alcohol), v e. sol. water, insol ether Its aqueous and alcoholic solutions are purple Not affected by HCl Alkalıs decompose it -Zinc salt (Č,H,N,S,Cl),ZnCl, aq

DI-METHYL-AMIDO-JUGLONE v. JUGLONE. METHYL-AMIDO-MESITYLENE v. METHYL-MESIDINE.

METHYL AMIDO METHYL-BENZENES v. METHYL-PHENYL METHYL AMINES

DI - METHYL - AMIDO - METHYL - PHEN-

elimination of the NH. group from 'tolylene red' by means of nitrous acid and alcohol (Bernthsen a Schweitzer, B 19, 2605) Red greenish glistening needles or flat prisms Has basic properties Dissolves in dilute acids with a violet colour, in cone H₂SO₄ with a reddish brown, which on dilution first becomes green, then blue, and finally violet Soluble in ether with a yel lowish-red colour and yellow fluorescence Sublımable

Di methyl di-amido methyl phenazine

$$C_{15}H_{16}N_4$$
 re $C_6H_3(NMe)$
 $\downarrow N$
 $C_6H_2Me(NH_2)$

Formed by oxidation of nitroso-Tolylene red oramido dimethyl aniline together with tolylene m diamine The leuco base has the formula $C_6H_s(NMe_2) < NH > C_8H_2Me(NH.)$ (Bernthsen a

Schweitzer, B 19, 2604)

DI METHYL AMIDO METHYL-QUINOLINE TETRAHYDRIDE Di-methylo di-iodide C₉H₉MeN NMe, Me₂I₂ [171°] Formed by heating $(\dot{P}y\ 1)$ amido quinoline tetrahydride with methyl alcohol and MeI (Ziegler, $B\ 21,862$) Crystals

METHYL-AMIDO METHYL-THIAZOLE

amine [42°] Formed by the action of chloroacetone on methyl thio urea (Traumann, A 249, 44) Crystalline but extremely hygroscopic, m sol ether Strongly alkaline in reaction When heated with HClAq in a sealed tube it yields methylamine Br completely decomposes it

Salts-B'HI small white needles, melts, when anhydrous, at 136° (T) —Platinochlor-ide orange yellow plates [167°]

Acetyl derivative C.H.AcN.S. [110°] White needles

Methyl-amido-methyl thiazole

SC(NH) >NMe Imido di methyl thiazole CH CMe

Formed from chloro acetone by treatment with ammonium sulpho cyanide (Tcherniak a Norton, B 16, 345) and heating with MeI the resulting amido methyl thiazole (socalled propinine sulphocyanide) (Hantzsch a Weber, B 20, 3122, 3336) Crystalline, but very hygroscopic Strongly alkaline When heated with HClAq in sealed tubes it yields ammonia Conc KOHAq has no action

Salts -B'HIaq Tables [164°] -Platinochloride orange tables [193°]

Acetyl derivative C,H,AcN,S [113°] White needles (containing 6 aq)

D1-methyl-amido-methyl-thiazole CH10N2S

S . C(NMe) NMe Methyl ımıdo dımethylthrazole [96°] Formed by adding conc KOHAq to its hydro-iodide (Hantzsch a Weber, B. 20, 8123) White needles, sol alcohol, water, and

ether Bromine reacts with formation of C₃MeBr(NMe₂)SN [114°]

Salts -B'HIaq [54°] From MeI and C₂MeH(NHMe)SN Melts at 155° when an hydrous

Methylo-rodide B'MeI

needles, v e sol water and alcohol
DI-METHYL AMIDO-NAPHTHOIC ACID C₁₀H_a(NMe₂)(CO₂H) [14] [165°] Formed by heating di methyl 'a) naphthylamine with COCl Formed by at 70° for 4 hours (Friedlander, B 21, 3126) Needles (from dilute alcohol), sol dilute acids and alkalis When acted upon by diazo com pounds the azo- group displaces the CO H — (HA'),H PtCl_s yellow needles

DI METHYL AMIDO-NAPHTHO-PHEN

AZINE C10H6 C₆H₂ NMe₂ $D_l methul$

[205°] Formed from ni naphth eurhodine troso di methyl aniline hydrochloride, (\$) naph thylamine, and AcHO (Witt, B 21, 720) Rhombic tables (from toluene or xylene), red by transmitted, and red or green, according to the faces, by reflected light, sol alcohol, ether and benzene, forming yellow solutions with yel low fluorescence Is volatile with slight decom position, and sublimes readily in woolly flocks. The violet red solution in conc. H SO₄ becomes successively black, green, grey, and blue vielet on dilution. The salts crystallise readily, have a bronzy lustre, and are dissociated by water AcHO dissolves it with red violet colour Conc HNO, with violet, soon becoming bright yellow and depositing the nitro compound

METHYL-AMIDO NAPHTHOQUINONE

 $\mathbf{C}_{11}\mathbf{H}_{0}\mathbf{NO}_{2}$ i e $\mathbf{C}_{10}\mathbf{H}_{5}\mathbf{O}_{2}(\mathbf{NHMe})$ [232°] Formed by adding a solution of methylamine acctate to an alcoholic solution of (a) naphthoquinone, evaporating nearly to dryness, adding water, and crystallising the pp from alcohol (Plimpton, C J 37, 639) Glittering red needles, v sol al Aqueous SO₂ at 150° forms an unstable cohol colourless reduction product

Di-methyl-amido-naphthoquinone

C₁₀H₅O₂(NMe₂) [118°] From (a) naphthoquinone and di methyl amine in alcoholic solution (Plimp Red needles

DI-METHYL AMIDO-NAPHTHYLAMINE vNAPHTHYLENE DI METHYL DIAMINE

TETRA-METHYL-DI-AMIDO-DI NAPH. THYL PHENYL-METHANE

Ph CH(C₁₀H₆NMe₂)₂ [189°] Formed by the action of benzoic aldehyde on di methyl (a) naphthylamine in presence of ZnCl2 (Friedlander, B 21, 3128) Colourless crystals, v sol HOAc, benzene, CS₂, and dilute mineral acids, sl sol alcohol, ether Does not yield a colour on oxi dation

Hexa methyl tri amido-di-naphthyl phenyl methane $HC(C_{10}H_6NMe_3)_2C_6H_4NMe_2$ [179°] Formed by condensing di-methyl p amido ben zoic aldehyde with di methyl (a) naphthylamine in presence of ZnCl₂ (Friedlander, B 21, 3129) White needles Does not yield a colour on oxidation

METHYL-AMIDO-NITRO- compounds v NI TRO-METHYL-AMIDO- compounds

METHYL-AMIDO-OXY- compounds v Oxy METHYL-AMIDO- compounds

METHYL-AMIDO PEREZONE v. METHYL-AMIDO PIPITZAHOIC ACID

METHYL o AMIDO-PHENOL Methylde rivative C₆H₁₁NO is C₆H₄(NHMe)(OMe) [1 2] Methyl anisidine (219°) Formed by mixing the methyl derivative of o amido phenol with MeI at 0° (Muhlhauser, A 207, 247) Oil -B', H PtCl, short yellow prisms, m sol water

Methyl-p amido phenol Ethylderivative C.H., NO ve C.H. (NHMe) (OEt) [14] (251°) Formed by heating the ethyl derivative of p oxy phenyl amido acetic acid at 260° (Bischoff a Nastvogel, B 22, 1789) SI sol water, v sol alcohol and ether -B'HCl needles

Di methyl o amido phenol C,HiNO ie Obtained, to $C_oH_1(NMe_2)(OH)$ [1 2] $[45^{\circ}]$ gether with McCl, by the dry distillation of the methylo chloride (Griess, B 13, 248) white prisms, v sl sol hot water, v sol alcohol, ether, HOAc, and aqueous KOH FeCl₃ gives a reddish violet colour Its hydrochloride is

Methylo hydroxide C,H,(NMe,OH)(OH)

aq Prepared by the action of

MeI and kOH on a solution of o amido phenol in methyl alcohol (Griess, B 13, 246) Prisms,

at 105° which become CoH. NMe, sol.

water and alcohol, insol ether Has an intensely bitter taste. On distillation it is converted into C,H,(NMe)(OMe) With acids it forms the -C,H,(NIe₃I)(OH) aq following salts Its solution, neutralised by soluble prisms ammonia, deposits sparingly soluble needles or

prisms of C,H4(NMe,I)(OH)C,H4< NMe₃

C_bH₄(NMe₃Cl)(OH) 2aq long soluble prisms — (C_bH₄(NMe₃Cl) OH) PtCl₄ yellowish red needles, sl sol cold water - The periodide forms brown insoluble leaflets - The nitroprusside (C H₁₃NO) H FeCy, NO forms crystals, sl sol cold

Methyl derivative C9H13NO 1e CH₄(NMe)(OMe) [12] (211°) SG 23 1 016 Formed by an isomeric change by distilling

(Griess, B 13, 248) Formed also NMe,

from MeI and the methyl derivative of o amidophenol (Muhlhauser, A 207, 248) Colourless liquid, with burning taste -B'2H2PtCl sparingly

soluble golden yellow prisms

Methylo rodide of the methyl derivative C.H.(NMe,I)(OMe) From the preceding and MeI Long white needles (G) or tables (M), sol hot water and hot alcohol With moist Ag2O it yields a strongly alkaline hy-It also yields a platinochloride (C, H, (NMe, Cl) OMe) 2PtCl,, which crystallises in sparingly soluble yellow plates or tables

C.H.(OH)NMe2 Di-methyl-m-amido-phenol Prepared by fusing di methyl amido benzene m sulphonic acid with KOH Also by heating resorcin with di methyl amine under pressure

EthyletherCoH4(OEt)(NMe2) [13] (247°) Obtained by boiling a solution of mamidophenetol and methyl iodide and slowly running

in the calculated quantity of potash is distilled over with steam (P Wagner, J pr [2] 32, 77, Baur a Stadel, B 16, 32) Converted by HCl and amyl nitrite into the nitroso compound C₆H₃(NO)(OEt)(NMe)

 $\hat{\mathbf{D}}_1$ -methyl-p-amido-phenol Methylo-

The anhydride CoH, hydroxide

is formed by the action of MeI and conc KOHAq upon p amido phenol in the cold (Griess, B 13, 250) Prisms or plates Changes on distillation into the isomeric C_eH₄(NMe₂)(OMe)[48°] Methyl derivative

C_sH₄(NMe)(OMe) [14] [49°] Formed as above (Griess, B 13, 249) Prisms or plates (from

C,H,(NMe,I)(OMe) Methylo rodide Formed by the action of MeI on either the methyl derivative or the methylo hydroxide Tables or plates With moist Ag O it yields the methylo hydroxide as a strongly alkaline mass. The platinochloride

(C₆H₄(NMe₃Cl) OMe).PtCl₄ forms small yellow

prisms, sl sol water

Di-methyl-di-amido-phenol Anhydride of methylo hydroxide CoH, NoO 16

∕0 $\sum_{\substack{\text{NMe},\\\text{by}}} \begin{bmatrix} 4 & 1\\ 2 \end{bmatrix}$ C6H3(NH2) Prepared by reduction

of the methylo hydroxide of nitro di methyl amido phenol with tin and HCl (Griess, B 13, 648) —B"H₂Cl₂4aq very soluble white plates —
B"H,PtCl₆2aq small prisms, sl sol water
TETRA-METHYL-DI-p-AMIDO-DIPHENYL
NMc, C₆H₄C₆H₄NMc₂ Tetra methyl benzidine

[195°] (above 360°)

Formation -1 By heating di methyl aniline (1 pt) with HSO, (4 pts) at 200° Formed also in small quantity by oxidising di methyl aniline by boiling with PbO, and dilute H SO, (Michlei a Pattinson, B 14, 2161, 17, 115) -2 By heating di methyl aniline with AlCl, in presence of air (Gnaud, Bl [3] 1, 692) -3 By methylation of benzidine

Properties - Colourless needles, sol hot, sl sol cold, alcohol Not volatile with steam Gives a green colouration with FeCl, or CrO, -B"H Cl. sparingly soluble needles -B"H.Br. ncedles -B"H I. white needles -B'H PtCl

Methylo vodide B"MeI [263°] Needles, sl sol water and alcohol Loses MeI when dis tilled with soda lime

[228°] B"MeCl Methylo caloride Crystals, very soluble in water and alcohol -B'MeClHPtCl, yellow pp Tetra methyl op di amido diphenyl

[2 1] NMe, C,H, C,H, NMe [1 4] Tetra methyl diphenyline [52°] (333°-345°) Formed by heating diphenyline hydrochloride with MeOH in sealed tubes at 180° (Reuland, B 22, 3015) Prisms Gives with platinic chloride an unstable pp Chloranil pr tion —B"C₂H (NO₂)₃OH Chloranil produces a blue coloura-H (NO₂)₃OH [200°] Red needles

Methylo iodide B"MeI [184°] Needles, v sol water, alcohol, and ether

Di methylo di-rodide B"Me,I, [196°]. Crystalline, v sol water and alcohol

Tetra-methyl tetra-amido diphenyl NMe, C,H,(NH,) C,H,(NH,) NMe, Tetra-methylbenzidine [1680] Prepared by reduction of dinitro tetra methyl diphenyl (Michler a Pattin son, B 14, 2165, 17, 118) White silvery plates, v sol hot alcohol, sl sol cold alcohol, insol water FeCl, gives a violet colouration K2Cr2O, and H₂SO, produce a brownish red colour-B"H₂Cl₂ (dried at 110°) sparingly solubl sparingly soluble colourless needles -B"H2I2 sparingly soluble needles -B"H2PtCl, yellow pp

Methyl α amido phenyl acetic acid C₉H₁₁NO₂ se C6H3 CH(NHMe) CO2H Formed from the nitrile of mandelic acid CoH, CH(OH) CN by digesting with alcoholic NH.Me at 70°, and de composing the resulting nitiile with HCl (Tiemann a Piest, B 14, 1982) Slende (from hot water) Sublimes at 274° Slender needles Sl sol cold water, insol alcohol and ether

Amide CeH, CH(NHMe) CO NH2 [155° Slender needles -B HCl Needles, sol alcohol,

msol ether

DI-METHYL-AMIDO-PHENYL-ω-AMIDO-CRESOL Methyl derivative [4 1] NMe, C,H, NH CH, C,H, OMe [1 4] [104°] Formed by reducing NMe, C,H, N CH C,H, OMe with sodium (Steinhart, A 241, 343) Light green plates, v sol acids, forming red solutions Its alcoholic solution decomposes rapidly

DI METHYL-AMIDO-DI PHENYL AMINE Me₂N C₆H₄ NHPh [130°] One of the products formed by the action of phenyl hydrazine on nitroso dimethylamine in an alcoholic solution (O Fischer, B 21, 2612) White needles (from petroleum-ether), v sol dilute HCl, m sol dilute SO,H, Gives a blue colouration with FeCl₃ Dissolves with a red colour in nitric acid

Nitrosamine C₁₄H₁₅N₃O [116°] Yellow

needles (from alcohol)

Tetra-methyl-di-amido-diphenyl-amine (NMe₂ C₆H₄)₂NH [119°] Obtained by oxidising a mixture of di methyl aniline (1 mol) and di methyl p phenylene diamine (1 mol) and reducing the resulting 'dimethyl-phenylene green' (Bindscheidler, B 16, 864) Yellowish dimetric tables

Hexa-methyl-tri amido triphenylamine Tri-methylo trichloride (NMe₃Cl C₆H₃),N Obtained by heating tri amido tri phenyl amine hydrochloride with MeOH at 190° (Heydrich, B White needles -19, 758)

(NMe,Cl C,H,),N 3PtCl

DÍ-MĚTHÝL AMÍDO-PHENYL-BENZYL-AMINE NMe₂ C₆H₄ NH CH₂Ph [48°] Obtained by reducing benzylidene di-methyl phenylene diamine [101°] with sodium amalgam (Kohler, A 241, 861) Yellowish plates, v sol dilute mineral acids, alcohol, ether, benzene, and petroleum ether

Nitrosamine NMe₂ C₆H₄ N(NO) CH₂Ph Slender yellow needles, sol alcohol

DI-METHYL - AMIDO - DI-PHENYL CAR. BINOL NMe2.C6H, CH(OH) C6H, Dr methyl-[70°] amido di-phenyl carbinol Formed by reducing di methyl amido benzophenone with sodium amalgam, or by the action of benzoic aldehyde on di methyl aniline (Albrecht, B 21, Thin white needles, insol water, v e sol ordinary solvents, sl sol petroleum ether

Di-methyl-di-amido di-phenyl-carbinol NMe₂ C₆H₄ CH(OH) C₆H₄ NH₂ [165°] Formed by carefully reducing p nitro di methyl amido di-phenyl-carbinol with zinc dust and HCl (Al-

brecht, B 21, 3295) Dissolves in HOAc with blue colouration Crystallises from benzene in needles containing benzene and melting at 142° Gives off water (1 mol) when heated above its melting point Boiling with zinc dust and HCl reduces it to di methyl diamido di phenyl methane [93°]

Tetra methyl di amido-di phenyl carbinol $C_{17}H_{22}N_2O$ te (NMe₂ C_6H_4)₂CH(OH) [96°] Ob tained by reducing tetra methyl di amido benzophenone in hot alcoholic solution with sodium amalgam (Michler a Dypertuis, B 9, 1899, Nathansohn a Muller, B 22, 1879) Colourless Nathansohn a Muller, B 22, 1879) triclinic prisms, v sol alcohol, HOAc, benzene, and ether Its solution in HOAc is blue, the benzene solution is colourless

Formed by passing HCl Salts -B"HCl into a solution of the base in ether Small colourless slender radially grouped needles air it turns blue and deliquesces It is dissociated by water —B"H₂PtCl_s minute yellow needles, v sol hot alcohol —B"C_sH₂(NO), OH minute yellow dank green crystalline mass, v sol hot alcohol, sl sol benzene, insol ether

Di methylo di-rodide B"Me₂I₂ [195°] Small plates (from alcohol), sl sol cold, v sol Dr methylo dr-rodide B"Me₂I₂ hot, alcohol and water, insol benzene and ether

Tetra-methyl di amido-tri-phenyl-carbinol C₂₂H₂₈N₁O is C₆H₅C(OH)(C₆H₄NMe₂)₂ [132°]
Malachite green Benzaldehyde green
Formation—1 By the action of dimethyl

aniline on benzotrichloride in presence of a metallic chloride (Doebner, B 11, 1238, 13, 2222) -2 By the oxidation of a slightly acid solution of tetra methyl di amido tri phenyl-methane with MnO or PbO_2 (E a O Fischer, B12,796), or with tetra chloro quinone (O I ischer, A 206, 130) -3 By heating di methyl aniline (4 pts) with BzCl (2 pts) and ZnCl₂ (3 pts) (Fischer)

From di methyl aniline Preparation - 1(2 mols), ZnCl₂ (half its weight), sand, and benzo trichloride at 100° The product is dis tilled with steam and the dye ppd from the aqueous residue by NaCl The pp is the zinc double chloride, which may be converted by KOH into the base This is conveited into the oxalate which may be purified by crystallisation from water and then decomposed by ammonia (Doebner, A 217, 250)-2 By heating benzoic aldehyde (40g) with dimethylaniline (100g) and 93 pc alcohol (40 g) over a water bath POCl (65 g) is then added gradually, and when cool the mass is extracted with warm water and the base ppd with NaOH The yield is nearly theoretical (Nencki, M 9, 1148) —3 By heating benzoic aldehyde with ZnCl₂ and di methylaniline, and oxidising the resulting leuco base with PbO₂ (Muhlhauser, D P J 263, 249)

Properties - Nearly colourless cubes V sol alcohol forming a green solution When freshly ppd it is v sol ether, but when crystalline it is sl sol ether, m sol CS, ace

tone, benzene or light petroleum

Reactions -1 HClAq at 250° splits it into dimethylaniline and di methyl p amido benzo phenone — 2 On reduction it yields leuco malachite green (tetra methyl di amido tri phenyl-methane) [101°] —8 Fuming HNO, in HOAc forms an amorphoushe xa nitro derivative

Salts-The salts of organic acids and

neutral salts of mineral acids are green and dye emerald-green They are v sol water, the oxalate being m sol water and the picrate sl sol water Concentrated mineral acids turn the solutions orange, forming acid salts Diluting with water restores the green colour In the cold, dilute acids dissolve the base, forming a nearly colourless solution, which turns deep green when heated, a molecule of water being probably split off. Thus the hydrochloride be-

comes C₆H₆ C_CC₆H₄NMe₂C₁

(C₂₃H₂₄N₂HCl)₁(ZnCl₂)₂2aq [c 130°] Malachite green Thick, dark green prisms, sol water (I'ischer, B 14, 2520) — C₂₃H₂₄N₂ZnCl₂aq — C₂₃H₂₄N₂H₂SO₄ — C₂₃H₂₄N₂H₂SO₄aq lustrous green prisms — (C₂₃H₂₄N₂)₂JH₂C₂O₄ Malachite Large green tables, sol water and — Picrates C₂₃H₂₄N₂C₆H₂(NO₂)₈OH water and alcohol - Picrates Golden needles (from benzene), insol water - $C_{23}H_{24}N_22C_6H_2(NO_2)_3OH$ golden needles

Di-methylo-di-iodide C₂₃H₂₄N₂Me₂I.aq [172°] Formed by heating the base with MeI and MeOH at 100° (Doebner) Green plates, sl sol alcohol, ether, benzene, CS2, and cold water, v sol hot water The same compound is ob tained by heating di p amido tri phenyl carbinol with MeI and alcohol at 120° (Doebner, B 15,

Ethyl dermative

C₆H₅ C(OEt)(C₆H₄NMe₂)₂ [162°] From the base by heating with alcohol at 110° (O Fischer, From the B 12, 1686)

Sulphonic acid C2, H2, (SO, H)N2O Green needles with reddish brown lustre, v e sol hot water, forming a green solution - NaA' MgA'2 4aq —CaA'2 3aq

Dernatues v Bromo, Chloro, Nitro, and ()X1 FETRA METHYL-DI AMIDO TRI-PHENYL-CAR

Tetra-methyl-ppo-tri-amido-tri phenyl-

carbinol C., H. N.O i e

 $NH_2 C_6H_4 C(OH)(C_8H_4NMe_8)_2$ [191°] Formed by oxidation of the acetyl derivative of the leuco base (tetra methyl di p amido o amido tri phenyl methane) with lead perovide and dilute H SO₄ (Fischer a Schmidt, B 17, 1892) (rlistening prisms (from ether) The salts are soluble in water with a bluish green colour

Tetra methyl tri p amido-tri phenyl carbinol $NH_2 C_8H_4 CH(OH)(C_8H_4NMe_2)_2$ Tetra methyl pararosaniline Obtained by oxidising the acetyl derivative of tetra methyl tri p amido tri phenyl methane with PbO, and boiling the resulting acetyl derivative with HCl (O Fischer a G Körner, B 16, 2904) Small crystals (from ether)

Penta-methyl tri amido tri phenyl carbinol C₄H₂₈N₄O₄e (NMe₂ C₆H₄)₂C(OH) C₆H₄NH Me Methyl violet [130°] Prepared by oxidising dimethylaniline with SnCl,, with ICl, with HgCl, and KClO, with KClO, and CuSO, or with NaCl and Cu(NO₃) (Lauth, Rep Chim app 1861, 345, Poirrier a Chappat, Bi [2] 6, 502, Hofmann, B 6, 357) Formed also by heating dimethyl aniline with CaH, SO, Cl at 100° (Hassencamp, B 12, 1275), and, together with formic aldehyde, by shaking hexa methyl tri amido tri phenyl carbinol with MnO, and dilute H,SO, (E a O

Fischer, B 11, 2097) Commercial methylviolet may be freed from admixed hexa methyltrı amıdo trı phenyl carbinol by boiling with ligroïn (Wichelhaus, B 16, 2006, 19, 108). Methyl violet occurs in Hofmann's violet

Properties - Brown powder, melting under water Insol water, ether, and ligroin Its alcoholic solution is violet Its solution in HCl is reddish violet, and is ppd by NaOH, but not by ammonia Reduced by ammonium sulphide to its leuco base Tin and HCl reduce it, form. ing a substance melting at 155° Boiling HClAq splits it up into di methyl aniline and tri-methyldi amido benzophenone

 $\begin{array}{c} {\rm Salts-Chloride} \ C_{24}H_{28}N_sCl \ \imath \ e \\ {\rm (NMe_2\ C_6H_4)_2C\ C_6H_4\ NMeHCl} \ \ Amorphous \ mass, \end{array}$

with green metallic lustre Its aqueous solution is violet, but on adding HCl it becomes first green, then deep yellowish brown It dissolves in alcohol Conc H SO, forms a yellow solution, which on dilution changes through greenish blue to violet It dve silk, wool, and mordanted cotton violet —C.,H.,N,I minute needles
Picrate C.,H.,N,C,H (NO.),(OH) Bronzed

needles (from alcohol)

Acetyl derivative Acetate (NMe₂ C₆H₄)₂C C₆H₄ NMeAc OAc [225°] From

methyl violet, Ac O, and NaOAc (O Fischer a. G Körner, B 16, 2905)

Hexa-methyl tri amido-tri phenyl carbinol C.3H31N3O1e (NMe, C6H4)3COH Crystal violet.

Hexa methyl para rosaniline [195°]
Formation —1 Together with its methylo

iodide, by heating methyl violet with MeI and MeOH at 120° (Hofmann, B 6, 363) -2 By the action of dimethylaniline on tetra methyl-diamido benzophenone in presence of dehydrating agents (Kern a Caro) In this reaction tetra methyl di amido thio benzophenone may aiso be used -3 By the action of COCl., of ClCO Et. or of ClCO CCl_s, in presence of ZnCl on di methylaniline - 4 By condensation of tetramethyl di amido-di phenyl carbinol with di-methylaniline and oxidation of the resulting leuco base -5 By gradually adding tetra chloroquinone (1 pt) to dimethylaniline (2 pts), and heating the product to 65° (Meister, Lucius, a. Bruning, B 13, 212, 2100, Wichelhaus, B 16, 2005) Perhaps the substance formed in this case is wholly or partially the penta methyl compound -6 By the action of COCl₂ or of ClCO, Et on dimethylaniline in presence of AlCl, (Hofmann, B 18, 767, Wichelhaus, B 19, 109)

Properties - Dark reddish violet monoclinis Needles containing benzene (from benzene) Insol water, sol ether, acetone, and ligroin, sl sol alcohol, v e sol chloroform and benzene. Boiling HClAq splits it up into dimethylaniline and tetra methyl di amido benzophenone Aqueous ammonium sulphide reduces it to hexamethyl tri amido tri phenyl methane

Salts - Chloride C25H30N3Cl 1e

(NMerC_eH₄)₂C C_eH₄ Hexagonal crystals, with greenish brown lustre (Wada, B 18, 768. Sol alcohol Forms a violet solution in water, which on adding HCl becomes first blue, then green, and finally yellow NaOH gives a violet Conc H.SO, forms a yellow solution,

changed on dilution through green and blue to violet Dyes silk, wool, and mordanted cotton bluish-violet —C₂₂H₃₀N₃Cl 8aq crystals, with bronze lustre —(C₂₂H₃₀N₃Cl)₂8PtCl₄ brickred crystalline pp, decomposed by water -C₂₅H₃₁N₃OH₂I₂ green crystals At 100° it gives off MeI, becoming the iodide of pentamethyl-tri amido tri phenyl-carbinol - Picrate $\mathbf{C}_{23}\mathbf{H}_{22}\mathbf{N}_{3}\mathbf{2C}_{6}\mathbf{H}_{2}(\mathbf{NO})_{3}\mathbf{OH}$ yellowish prisms, with coppery lustre

 $Methylo-rodide \quad C_{25}H_{81}N_8I_2MeI$ pararosaniline, MeI, and MeOH at 115° (Hof

mann, B 6, 365)

TETRA-METHYL-DIAMIDO-DIPHENYL-

CUMYL-METHANE C₂₆H₂₂N₂ ie (NMe₂ C₆H₄)₂CH C₆H₄C₃H₇, Prepared by heating cuminic aldehyde with dimethylaniline and ZnCl₂ to 120°, the yield is about 80 pc oxidation it gives a dye stuff closely resembling malachite green

Salts—B"H₂Cl₂ white crystalfine powder—B"(C₆H₂(NO₂)₃ÔH)₂ green crystals, [156°], explodes at 220°—B"H₂Cl₂PtCl₄ yellow crystals green crystals, [156°],

Methylo rodide B"Me,I, white needles [220°] Si sol cold, v sol hot, water (Zeigler, B 13, 786)

DI - METHYL - AMIDO - PHENYLENE - DI -PHENYL-DIKETONE NMe₂ C₆H₁(CO C₆H₃)₂ [55°] From dimethylaniline and BzCl at 180° Crystals, v sol alcohol and ether

Hexa - methyl - tri - amido - phenylene - di-

phenyl-diketone C₂₆H₂₉N₃O₂ 1 e $\mathrm{NMe_2C_oH_3(CO\ C_oH_1\ NMe_2)_2}$ [122°] From boiling di methyl aniline and $\mathrm{COCl_2}$ (Michler, B 9, 716, Michler a Dupertuis, B 9, 1899) Monochinic crystals, a b c = 587 1 714, β = 125° 18′ METHYL - AMIDO - PHENYL - ETHANE Nitroso derivative [41]Et C.H. NMe NO [162°] Formed from di methyl amido phenyl ethane, HCl, and NaNO2 (Heumann a Wiernik, **B** 20, 2423) Needles, insol water, sl sol ether and cold alcohol Zinc and HOAc reduce it to ethylphenyl-methyl hydrazine, the acetyl deriva tive of which melts at 68°

Di-methyl-amido-phenyl-ethane

[4 1]Et C₆H₄ NMe₂ [89°] Formed, together with hexa methyl tri amido tri phenyl methane, by heating glycol (1 mol) with dimethylaniline (2 mols) and ZnCl₂ at 100°-120° (H a W) Needles or prisms (from alcohol), v sol ether, warm alcohol, and benzene, insol water Its salts are deliquescent, and its platinochloride is unstable

stable Oxidising agents colour it blue Methylo-rodrde Et CaH, NMe3I p amido phenyl ethane and MeI (Hofmann, B 7, 527)

Tetra-methyl-d1-amido-d1-phenyl-ethane $C_{18}H_{24}N_2$ 2 c NMe₂ C_8H_4 $C\dot{H}_2$ $C\dot{H}_2$ C_8H_4 NMe₂ [50°] (over 300°) Prepared by heating ethylene bromide with dimethylaniline at 100° (Schoop, B 13, 2196) Slender needles, sol ether. ligroin, hot wood spirit, and alcohol, insol water With FeCl, it gives a green colouration, and finally quinone But it does not yield a and many quinone but it does not plead a dye on oxidation—B"H₂I₂ Sol water and alcohol — Oxalate B"2H₂C₂O₄ — Picrate B"C₂H₂(NO₂)₂OH yellow pp, sol hot alcohol Methylo sodide C₁₈H₂₄N₂MeI From diamido-di-phenyl-ethane, MeI, and a little KOH

at 150°-180° (Heumann a Wiernik, B 20, 909)

Tetra-methyl-di-amido-tri-phenyi-ethane C.H. CMe(C.H. NMez), This is the chief pro duct of the action of acetophenone on dimethyl aniline in presence of ZnCl2 (Doebner a Petschoff, A 242, 339) Yellow oil, v sol ether, benzene, petroleum ether, and hot alcohol It boils above 360° with partial decomposition It is not vola tile with steam

Hexa-methyl-tri-amido-tri-phenyl-ethane NMe₂ C₆H₄ CH₂ CH₂ CH₄ NMe₂)₂ [125°] Formed by heating CH₂Cl CHCl, with dimethylaniline and ZnCl₂ at 110°-120° (Heumann a Wiernik, B 20, 2424) White needles, insol water, v sl sol cold, sl sol hot, alcohol, v sol ether With PbO₂ and HOAc it gives a greenish blue colour

Octo methyl-tetra amido-tetra-phenyl ethane C₃₄H₄₂N, 16 (NMe₂C₆H₄)₂CH CH(C₆H₄NMe₂)₂ [90°] (300°) Formed by heating acctylene tetra bromide with dimethylaniline at 100° (Schoop, B 13, 2199) Prisms, sol alcohol, ether, and benzene, insol water With FeCl, or CrO, it produces quinone —B"2H,PtCl, yellow amorphous pp - Picrate B"C₆H₂(NO₂)₃OH yellow plates, sol hot water

Deca-methyl-penta amido-penta-phenylethane C₂H(C₈H₄ NMe₂)₅ [184°] Formed by heating a mixture of dimethylaniline (50 g), chloral hydrate (20 g), and ZnCl (10 g) at 100°, the yield being 10 g (O Fischer, B 11, 951, A 206, 120, Boessneck, B 18, 1516) Colourless needles (containing aq) (from alcohol), v sol chloroform Sol benzene, v sl sol alcohol and ether On oxidation it gives a green ish blue dyestuff

DI-METHYL - a - AMIDO - wa DI-PHENYL ETHYL ALCOHOL NMe CHPh CHPh OH [110°1 From NH, CHPh CHPh OH, MeI, and EtOH (Goldschmidt a Polonowska, B 20, 494) White needles —B'2H2PtCl3 2aq

DI METHYL AMIDO PHENYL ETHYL DI THIO CARBONATE EtO CS SC₆H₄NMe₂ [54°] Formed from di methyl p phenylene diamine by diazotising and heating the product with aqueous potassium xanthate at 70° (Leuckhart, J pr [2] 41, 206) Light yellow crystals, insol water, sol ordinary menstrua With alcoholic potash it gives S(C,H,NMe,)2

TETRA-METHYL DI AMIDO-DI PHENYL FURFURYL METHANE C.4H.3O CH(C,H N Me)2 [83°] Prepared by the action of furfuraldehyde on dimethylaniline (O Fischer, B 11, 950)

DI-METHYL-AMIDO PHENYL GLYOXYLIC ACID C10H11NO, te NMe2 C6H4 CO CO H [187°] Obtained by saponifying its ethyl ether which is produced by adding Cl CO CO2Et to dimethylaniline at 100° (Michael a Hanhardt, B 10, 2081) Small plates or needles Sol water and alcohol -NaA' (dried at 150°) Small needles. -BaA'₂ (dried at 150°) Plates

Ethyl ether EtA' [95°] Yellow plates (from alcohol) Cannot be distilled

TETRA METHYL DI-AMIDO DI PHENYL-HEPTANE (NMe₂ C₆H₄)₂CH C₆H₁₅ [59 5°]. mm) Formed from dimethyl-(275° at 15 mm) aniline, heptoic aldehyde (cenanthol) and ZnCl, (Krafft, B 19, 2987) Crystalline solid, not readily oxidised -B"H_PtCl, yellow crystalline pp, v sl sol water and ether alcohol

D) METHYL - AMIDO - PHENYL - IMIDO - | QUINOLINE TETRAHYDRIDE THIOSUL-PHONIC ACID

 $N C_4H_3(NMe_2) S SO_3H$ Formed

by oxidising a mixture of quinoline tetrahydride (1 mol) with di methyl p phenylene diamine thio sulphonic acid (1 mol) by K₂Cr₂O₇ (Lell mann a Boye, B 23, 1374) Small lustrous green needles, sl sol water Changes after some time to a brown powder Zinc dust and HCl reduce it, and the product yields a blue dye on oxidation

DI METHYL AMIDO PHENYL HEXYL KE TONE C15H 3NO 1 e NMe C6H4 CO C6H13 [49°] (190° at 20 mm) Formed, together with the leuco base C. H_{3.}N, by adding heptoyl chloride to a mixture of ZnCl₂ and dimethylaniline (Krafft, B 19, 2987, Auger, Bl [2] 47, 44) Colourless needles Gives with conc HNO, a compound C_6H_{13} CO $C_6H_3(NO_2)(NMe_2)$ nıtro [65°]

Oxim NMe. C.H. C(NOH) C.H.12. [99°]. Colourless leaflets

DI METHYL DI AMIDO DI PHENYL KE-TONE v DI METHYL DI AMIDO BENZOPHENONE

MERCAP DI METHYL AMIDO PHENYL (260°) TAN NMe, C,H, SH [28°] Obtained by reducing tetra methyl di amido di phenyl sulphide with tin and HCl (Merz a Weith, B19, 1575, Leuckart, *J. pr.* [2] 41, 207). Old Dissolves in NaOHAq. Re oxidised by air to (NMe, C₆H₄) S. [118°]—Pb(SC₈H₁₀N). plates

Di methyl di amido phenyl mercaptan C_8H_1 N.S i.e. C_8H_2 (NMe)(NH.)(SH) [4 1 2] Formed by reducing methylene red (Jacobsen, B 21, 3104, Bernthsen, A 251, 1) Gives a diazo sulphide $C_6H_3(NMe) < \frac{N}{S} > N$ [78°] LeCl, gives a blue colouration With AcCl in benzene it gives the hydrochloride of ethenylamido dimethylamido phenyl mercaptan

 $NMe_2 C_6H_3 < N > CMe - Zn(C_8H_{11}N.S)_2$

DI-METHYL AMIDO DI PHENYL ME-THANE NMe, C,H, CH, C,H, This is perhaps the base, boiling at 335°, produced by heating di methyl aniline benzylo chloride in a sealed tube at 230° (Michler, B 10, 2079)

Dı methyl dı amıdo-dı phenyl methane NMe, C₆H₄CH₂C₆H₄NH₂ [93°] Formed by boiling p nitro di methyl amido di phenyl carbinol with zinc dust and HCl (Albrecht, B 21, 3296) Colourless needles, coloured bluish violet by PbO, or by tetra chloro quinone

Tetra methyl-di p amido di phenyl methane

Formation — 1 By heating methylene iodide, CHCl, of CO, Dochner, B 12, 810, cf Hanniman, B 10, 1235) -2 By heat ing methylal $CH_2(OMe)_2$ (1 mol) with dimethylar land (2 mol) with dimethylaniline (2 mols) in presence of ZnCl, to 120° (O Fischer, B 12, 1689, A 206, 117), or by acting on a mixture of methylal and dimethyl aniline with cone HClAq (Tröger, J pr [2] 36, 237) —8 One of the products of the action of acetophenone or of di ethyl ketone on dimethylaniline in presence of ZnCl₂ (Doebner a Pet-schoff, A 242, 888) —4 By heating dimethyl-

aniline with CCl, SO, Cl at 100° (Michler a Moro, B 12, 1170) -5 One of the products of the action of (a) naphthylamine sulphonic chloride on dimethylaniline (Michler a Salathé, B 12, 1789) -6 From C₂Cl₈, dimethylaniline and ZnCl₂ (Heumann a Wiernik, B 20, 2426) -7 One of the products of the action of zinc and HCl on a mixture of dimethylamline and CS₂ (Wiernik, B 21, 3204, cf Truger, J pr [2] 36, 241) —8 By distilling tetra methyl di amido benzophenone (1 pt) with zinc dust (10 pts) (Nathansohn a Muller, B 22, 1882) -9 A pro duct of the action of Ac O on dimethylaniline (Reverdin a De la Harpe, B 22, 1006) -10 The chief product of the action of methyl hexvl ketone on dimethylaniline (Doebner a Petschoff, A 242, 342) -11 By distilling tetra methyldi amido thio benzophenone with zinc dust (Baither, B 20, 1737)

Properties - Four sided tables or glistening leaflets (from alcohol) Insol water, sl sol cold, m sol hot, alcohol, v sol benzene, ether, Not volatile with steam On oxida and CS tion with HOAc and MnO₂ it gives a fugitive blue colour When boiled with MnO and H SO, it yields quinone Its alcoholic solution is turned blue by boiling with tetra chloroquinone It may be oxidised to tetra methyl diamido benzophenone (N a M) Conc HNO, in HOAc forms a tetra-nitro derivative which de composes at 218° With tri nitro benzene it forms a compound C₁ H N C₆H₂(NO), [114° and with m di nitro benzene a compound (C₁ H₂N) C₅H₄(NO₂)₂ [74°] (Van Romburgh, R T C 7, 226)

Salts -B"H.L. B".C.H.(NO),OH [178°], sparingly soluble tables

Methylo rodide B"Me.I. [214°] Yellow plates, v sol hot water and alcohol, insol ether (D a P)

Tetra - methyl - ero - pp - tri - amido - diphenyl methane (NMe, C,H,),CHNH, [135°] Obtained by reducing the imide of tetra methyldi amido benzophenone (auiamine) with sodium amalgam (Græbe, B 20, 3265) Colourless crystals, v sl sol water, m sol alcohol Gives an intense blue colouration with HOAc

Methyl cao amido tri phenyl methane CooHis N & C (CoH.) C NHMe [73°] Obtained by passing methylamine into a hot solution of Ph,CBr in benzene (Hemilian a Silberstein, B 17, 745) Prisms (from ligroin) Insol water, v sol alcohol -B.H.PtCl, 6aq -B',I Ppd as lustrous blue black needles by adding iodine to its solution in CS

Di methyl-cxo amido tri phenyl-methane C. H. N & C (C. H.s), C\Mez [97°] From erobromo tri phenyl methane and NHMe, in benzene (H & S) Insol water, v. sol alcohol -B'.H.PtCl

Di-methyl amido tra-phenyl-methane C21H21N

s.e (C₆H₅)₂CH C₆H₄NMe₂ [132°]
Formation -1 By heating di phenyl car binol with di methyl aniline and P2O, at 150° (O Fischer, B 11, 951 12, 1690, A 206, 114) 2 By heating benzophenone chloride Ph.CCl. with dimethylaniline and ZnCl, (F., cf Pauly, A. 187, 209)

Preparation — Benzophenone (10 g), dimethylaniline (13 g), and zinc chloride (10 g) are heated in sealed tubes for ten hours to 190° After driving over excess of dimethylaniline and benzophenone the residue is extracted with ether, and after distilling this off the base is recrystallised from alcohol (Doebner a Petschow,

Properties - Colourless needles, sl sol alcohol, v sol ether and benzene Does not give Is a weak a colouring matter on oxidation base, and does not combine with HOAc

Salts -B'HCl -B',H,PtCl needles, sl sol hot water

Methylo - rodide C, H, NMeI [186°]

Large white plates

Tetra-methyl-di-amido-tri-phenyl methane

C₂₁H₂₂N₂ • e (NMe, C₂H₄), CH C₂H₃, Leuco base of malachite green [102°] and [94°]

Formation — 1 By heating a mixture of benzoic aldehyde (10 pts) and dimethylaniline (23 pts) with ZnCl₂ The yield is 90 pc (O (23 pts) with ZnCl, The yield is 90 pc (O Fischer, B 10, 799, 1624, 11, 950, 2274, 12, 1685, A 206, 122) — 2 From benzylidene chloride, dimethylaniline, and ZnCl. -- 3 By heating di-amido tri phenyl methane with MeI and MeOH at 130° (F) -4 By heating its carboxylic acid (di methyl - aniline phthalin) (NMe₂ C₆H₄)₂CH C₆H₄ CO₂H with barium hydroxide -5 From tetra - methyl di amido tri phenyl-carbinol (malachite green) by reduction with zinc-dust and HCl (Doebner, B 11, 1239, A 217, 256) -6 A by-product in the action of phthalyl chloride and in that of benzoyl chloride on dimethylaniline — 7 By heating phenylglyoxylic acid with dimethylamiline and ZnCl, (Peter, B 18, 539)—8 A by product in the action of ZnCl, on a mixture of dimethylamiline and acetophenone (Doebner a. Petschoff, A 242,

Preparation —A mixture of benzoic aldehyde (40 g), dimethylaniline (100 g), and 93 pc alcohol (40 g) is heated on a water bath, and POCl_s (65 g) added slowly The product is ex tracted with water, the filtrate ppd by soda and the pp recrystallised from alcohol (Nencki, M 9, 1148)

Properties - Crystallises from benzene in (apparently triclinic) needles, melting at 102°, and from alcohol in triclinic leaflets, melting at 94° (E a O Fischer, B 12, 796) Insol water, v sol ether and benzene, sl sol petroleum In small quantities it can be distilled. Its salts are oxidised by MnO2 or PbO2 to malachite green Nitric acid forms a hexa nitro derivative [200°] When distilled with zinc dust it is reduced to aniline, dimethylaniline, and p amido di-phenylmethane (Manns, C C 1888, 1363)

Salts -B"H2Cl2 colourless hygroscopic needles, v sol water Gives off HCl at 100°, becoming B"HCl -B"H2PtCl, white pp, soon becoming yellowish green -The aurochloride is a golden-yellow floculent pp—Picrate B"2C₆H₂(NO₂)₃OH [220°] Aggregations of Aggregations of needles, m sol water

[218°-Di-methylo-di-rodide B"Me2I2 222°] (F), [231°] (Doebner, B 13, 2228) Plates, tables, or leaflets, v sol water Decomposed on fusion into MeI and the base

Tetra - methyl - ppo tri - amido-tri - phenyl-methane ([4 1]NMe₂ C₅H₄)₂CH C₅H₄NH₂ [1 2] [185°] o-Amido-leuco-malachite green Formed by reducing, by means of zinc-dust and HCl, the

product of the condensation of o nitro benzois aldehyde with dimethylaniline (Fischer a Schmidt, B 15, 683, 17, 1891) Colourless crystals (containing C₂H₆) Gives a reddish Colourless brown dye stuff on oxidation

Acetyl derivative C₁₉H₁₈(NMe₂)₂(NHAo).
[186°] Ghistening crystals Gives on oxidation (NMe₂ C₂H₄)₂ C(OH) C₂H, NHAc
Tetra-methyl-tri-amido-tri phenyl-methane

 $C_{23}H_{-7}N_3$ to $(NMe_2C_6H_4)_2CHC_6H_4NH$ Prepared by dissolving tetra methyl di pp amido di phenyl carbinol (20 pts) in HClAq (12 pts of S G 1 18) and water (100 pts), heating to 100°, and adding aniline hydrochloride (10 pts) (Nathansohn a Muller, B 22, 1886) Small needles (from warm alcohol), v sol alcohol, ether, and benzene, unsol water According to analogy it should be identical with the prece ding body With MeI it gives CH(C,H, NMe,I), [1720]

Salts -B"H2Cl2 yellowish green crystalline pp, got by adding HCl to an ethereal solu tion of the base V sol hot alcohol, sl sol ether, insol benzene -B"H,PtCl, light yellow flocculent pp, v sl sol water and alcohol—Picrate B"C₆H₂(NO₂)₃OH light green flocculent pp , v sol hot alcohol, insol benzene and ether

Benzoul derivative

(NMe, C,H,),CH C,H, NHBz [128°] Small, slender blue plates (from warm alcohol), v sol hot alcohol and benzene, sl sol ether, insol water

Tetra - methyl - ppm - tri amido tri phenyl methane ([4 1] NMe₂, C₆H₄) CH C₆H₄ NH [1 3] [130°] Prepared by reducing m nitro tetra methyl-di amido tri phenyl carbinol (E a O Fischer, B 12, 803) Colourless prisms or Gives a green dye on oxidation needles

Tetra-methyl tri p amido tri phenyl methane C₂₈H₂₇N₃te ([4 1] NMe₂ C₆H₄) CH C₈H₄ NH [1 4] [152⁵] Prepared by reducing the hydrochloride of p nitro tetra methyl di-p amido tii phenyl methane with zinc dust (Fischer, B 14, 2527) Colourless plates, sl sol alcohol Gives on oxi dation tetra methyl pararosaniline, a reddish violet dye

Acetyl derivative [108°] Needles Yields on oxidation the corresponding carbinol, a splendid green dye (Fischer a German, B 16, 708

Penta methyl tri p amido tri phenyl methane C24H29N, ie (NMe C4H4), CH C6H4 NMeH [116°] Obtained by heating penta methyl para rosaniline with alcoholic ammonium sulphide at 100° (Hofmann, B 6, 360, E a O Fischer, B 12, 799, Fischer a Körner, B 16, 2906) Large colourless needles (from alcohol) Sl sol hot water, v sol alcohol and ether - B",3H,PtCl,

Acetyl derivative [143°] Hexa-methyl-tri-amido-tri phenyl methane C₂₂H₃₁N₃ re HC(C₃H₁NMe₂), Hexa methyl-paraleucannine [178°] Formation —1 By treating chloral with di-

methylaniline and ZnCl₂ (E a O Fischer, B 11, 2097) The base so prepared melted, however, at 250°—2 From orthoformic ether (1 pt) and di methylaniline (31 pts.) at 100° (Fischer a Knorr, B 17, 98) —3 By condensation of p di methyl-amido benzaldehyde with di methyl aniline in presence of dry HOl gas or ZnOl, (Boessneck, B 19, 366)—4 From glycol, dimethylaniline, and ZnCl, at 100°-120° (Heumann a Wiernik, B 20, 2421) Needles or prisms When oxidised with MnO2 and H2SO4 it gives formic aldehyde and methyl violet (Fischer)

Tri methylo-tri rodide O2 H. N.I. 16. CH(C.H. NMe.I): [185°] From tetra- and hexa methyl-tri-p-amido-tri-phenyl methane, MeI, and MeOH at 100° (Hofmann a Girard, B 2, 448, Fischer, B 12, 2344) Yellow needles (containing aq), decomposes and becomes dark blue on fusion Gives (C₂₂H₄₂N₂Cl₂),3PtCl₂2aq Hexa methyl opp (?)-tri-amido-tri pnenyl-

Tri methylo tri-odide CH(C,H,NMe,I), [172°] Cotained by heating the corresponding tetra methyl tri am. c tri phenyl methane with MeI (Nathansohn a Muller, B 22, 1987) Small brown needles (from warm alcohol), v sol alcohol and hot water, almost

insol ether and benzene

Hexa-methyl mpp tri-amido-tri-phenyl-thane Tri methylo tri-iodids methane [3 1] NMe₃I C₆H₄ CH(C₆H₄ NMe₃I[1 4])₂. Formed by heating the base C23H27N2 or the corresponding CH(C.H. NH.), with Mel and MeOH at 120° (Fischer, B 12, 802, 13, 673) Crystallises with

difficulty, and is v e sol water Gives rise to 8PtCl,2CH(C,H,NMe,Cl), CHLORO NITBO-, and References - CHLORO-,

NITRO-, METHYL AMIDO PHENYL METHANES

TETRA METHYL DI AMIDO TRI PHENYL-METHANE CARBOXYLIC ACID C24H20N2O2 16 (NMe, C,H,),CH C,H, CO,H Di methyl aniline phthalin [200°] Obtained by treating di methyl amido phthalide with zinc-dust and HCl (Fischer, A 206, 101) Formed also by treating p aldehydo benzoic acid with dimethylaniline and ZnCl₂ (Low, 4 231, 367) Plates (from al cohol), v sol ether sl sol ligroin, m sol Conc H₂SO, forms a bluish violet Its zinc salt melts at 147° (L) alcohol solution C2.H2.N2O2H.PtCl2. -- Platinochloride

Piciate C,H,N O,C,H (NO,),OH
TETRA METHYL DI AMIDO TRI PHENYL METHANE CARBOXYLIC ALDEHYDE

C,H,N,O te (NMe, C,H,)2CH C,H, CHO From terephthalic aldehvde, dimethylaniline, alcohol, and ZnCl, (Löw, A 231, 381) Needles (from chloroform) Si sol alcohol, m sol benzene, v sol chloroform Its phenylhydrazide melts at

DI METHYL AMIDO PHENYL (a) - NAPH-

THYL SULPHONE CiaH, NSO, we Formed, together with NMe, CoH, SO, CoH, tetra methyl di amido di phenyl methane, by heating dimethylaniline (2 mols) with the oblor ide of naphthalene (a) sulphonic acid (Michler a Salathé, B 12, 1789) Crystals, v sol alco-Cone HClAq at 180° splits it hol and ether up into naphthalene, H₂SO₄, aniline, and MeCl Zinc and H₂SO₄ give dimethylaniline and naphthyl mercaptan Fuming HNO, gives tetra nitro methyl aniline and nitro naphthalene sul phonic acid

Di-methyl-amido-phenyl (3)-naphthyl sul-Resembles the preceding body in its mode of preparation, properties, and decompo

sitions (M a. S)

DI-METRYL p-AMIDO - PHENYL - OXAMIC mann, B 9, 845) Formed also as a by product, ACID C₁₁H₁₁N₂O₁ • • NMe₂C₂H₄ NH CO CO₂H. in the action of PCl₂ on dimethylaniline in [192°]. The ethyl ether is formed by boiling di-presence of AlCl₂ (S a M.) Colourless needles. Vol. III

methyl-p-phenylene diamine with oxalic other. and separated by solution in alcohol from the accompanying tetra methyl di amido-di phenyl oxamide (Sendtner, B 12, 530) The ether is then saponified by alcoholic KOH. Needles

(from water) or plates (from alcohol)

Ethyl ether EtA' [117°] Ye [117°] Yellow plates

or needles, v sol warm alcohol

DI-METHYL-AMIDO-PHENYL-OXAMIDE C₁₀H₁₂N₂O₂ 16 NMe₂ C₆H₄ NH CO CO NH₂ [259°] Formed by treating di-methyl amidophenyl-oxamic ether with alcoholic NH, (Sendt ner, B 12, 532) Nodules (from alcohol) --B'2H2SO, crystals

Tetra-methyl-dı amıdo-dı phenyl oxamıde NMe₂ C₄H, NH CO CO NH C₄H₄ NMe₂ Formed as described under di methyl amido phenyl oxamic acid (Sendtner) Small yellow needles, insol water, sl sol boiling alcohol Does not melt at 270° Diacid base, forming salts soluble

in water

TETRA-METHYL-DI-AMIDO-DI-PHENYL OXIDE C1.4H20N2O s.e (NMe2 C4H4)2O [119°] Formed by boiling the corresponding sulphide ('thiodimethylaniline') with an ammoniacal alcoholic solution of AgNO, (Holzmann, B 21, 2056) Stellate groups of colourless needles, insol water, sl sol cold alcohol, ether, and benz-Readily soluble in acids Conc HClAq at 200° gives MeCl and aniline -B"H2PtCl4 minute bright yellow plates, sl sol hot alcohol Picrate B"2C_eH₂(NO₂)_eOH [150°] Sma [150°] Small yellow needles, al sol cold alcohol and benz-

Tetra methyl di amido di phenyl-di-oxide NMe C₆H₄) O... Di oxy di methyl aniline [91°] Obtained by adding (4 mols of) silver nitrate to an alcoholic solution of tetra methyl di amido di phenyl di-sulphide (NMe2-CaH4)2S. (1 mol) treated with conc NH, It is also formed by the action of Fe,Cl, upon the conc HCl solution of the same base Thin silky needles, or plates V e sol alcohol, ether, and benzene, sol hot water It dissolves in acids, but its salts are not crystalline (Merz a Weith, B 19, 1573)

TETRA METHYL DI-AMIDO DI PHENYL-OXINDOLE C24H23N4O 1 6

 $C_6H_4-C(C_6H_4NMe_2)_2$

Di methyl aniline-NH - CO

[234°] Formed by heating isatin with isatin dimethylaniline and ZnCl, (Baeyer a Lazarus, B 18, 2642) Glistening colourless prisms SI sol ether, alcohol, and ligroin, insol water Dissolves in soids On oxidation it gives a splendid bluish green dye stuff

DI METHYL AMIDO TRI PHENYL-PHOS-PHINE C, H, NP 16. NMe. C.H. P(C.H.) [152°] Formed by the action of sodium on a mixture of chloro benzene and NMe, C, H, PCl, (Schenk a Michaelis, B 21, 1502) Colourless crystals, v e sol benzene, sl sol alcohol and ether Weak base, being almost entirely ppd by wate, from its solution in HClAq

Hexa methyl tri-amido tri phenyl-phosphine (NMe, C,H,),P [273°] Formed by heating dimethylaniline with PCl, in a sealed tube (Haniwhich turn blue on exposure to air V e sol chloroform, v sol dilute HClAq, m sol hot alcohol

DI . METHYL - AMIDO - PHENYL PHOS -PHINOUS ACID v DI METHYL AMIDO BENZENE PHOSPHINIC ACID

TETRA-METHYL-DI-AMIDO-DI-PHENYL-

PHTHALIDE C24H24N2O2 t. 6

 $(NMe_2, O_0H_4)_2C < \overset{O_0H_4}{O} > CO$ Dimethylanilinephthalein [191°] Prepared by heating dimethylaniline with ZnCl, and phthalyl chloride or phthalic anhydride (O Fischer, B 9, 1753, 10, 952, 12, 1691, A 206, 92) Colourless pointed crystals, insol water, v sol benzene, v sl sol Reduced by zinc dust and HOAc to tetra methyl di amido tri phenyl methane carboxylic acid (dimethylaniline phthalin) Potashfusion gives dimethylaniline, HOBz, and phthalic acid HNO, gives a hexa-nitro-derivative which decomposes at 230°

Salts -B"HCl small needles, m sol water -B"H2Cl2 hygroscopic crystalline mass, got by passing HCl into the ethereal solution Gives off HCl (1 mol) at 100° —B"₂H₂PtCl₆ crystal line pp —B"H₂PtCl₆ aq prisms — Picrate line pp B"H2PtCl_s aq B"2C_sH₂(NO₂)₂OH

Methylo-rodide B"Me₂I₂ [c 185°] Phthal green C₂₄H₂₄N₂O₂. This substance, isomeric with the preceding, is also formed in the action of phthalyl chloride on di methylaniline in presence of ZnCl₂ (Fischer) Îts hydrochloride, B"HCl, forms greenish yellow needles, m sol water Its zinc double salt crystallises in brass yellow needles which form a green solution in water Zinc and HCl reduce it to a leuco- base $C_{24}H_{24}N_2O$ which crystallises in small prisms [286°], and is easily re-oxidised to phthal green

TETRA METHYL-DI-AMIDO PHENYL-DI-PHENYLENE-OXIDE-CARBINYL CHLORIDE

C₆H₅ O C₆H₂NMe₂ O Tetra methyl-rosam-

Formed from benzotrichloride and dimethyl-m amidophenol at 50°-60° (Heumann a Rey, B 22, 3002) Dark red flocculent pp, strongly fluorescent in acid or neutral solution H₂SO₄ dissolves it giving an orange yellow colour, becoming dark-red on addition of water Silk and wool are dyed in feebly acid bath rose to bluish red

Salts -B'HCl dark red needles with steelblue reflex, v sol water and EtOH forming solu tions with a splendid blue red colour, and yellow fluorescence — (C₂H₂N₂OCl)₂PtCl₄ dark-red pp DI-METHYL-AMIDO-PHENYL-PROPANE

C₁₁H₁₇N i e NMe₂ C₆H₄ CH₂ CH₂ CH₃ methyl amido propyl benzene (230°) From p bromo-di methyl-aniline, propyl bromide, and sodium (Claus a Howitz, B 17, 1327) Oil

Methylo-rodide NMe I C.H. Pr [168°] Tetra-methyl-di-amido-di-phenyl-propane (NMe₂C₆H₄)₂CMe₂ [88°] From acetone (1 mol), dimethylaniline (2 mols), and ZnCl₂ (Doebner, B 12, 813) Long needles
DI-METHYL - AMIDO - PHENYL - QUINON -

IMIDE C, H, N,O 66

imide to a solution of di methyl aniline in concentrated aqueous oxalic acid (Fogh, B 21, 889). Formed also by the action of NaOH on di methyl phenylene green (Möhlau, B 18, 2914) Black crystals (containing $\frac{1}{3}$ aq) Yields, when treated with hot dilute HClAq, quinone and dimethyl phenylene p diamine May be reduced to a leuco- base

Sulphonic acid

o. SO,H C,H, Formed by passing M C.H.NMe2"

chlorine into amido phenol sulphonic acid suspended in water, and then adding di methylannline (F) Slender needles, v sl sol hot alcohol, in ol cold water and ether Its alka line solutions are blue Conc H₂SO₄ forms a cherry red solution

TĚTRA-METHYL DI-AMIDO DI PHENYL SULPHIDE (NMe₂.C₆H₄)₂S Thiodimethylan: line [126°] Formed by heating dimethyl aniline with persulphocyanic acid or SCl, (Tursini, B 17, 584, Holzmann, B 20, 1640, 21 2056, Michaelis a Godchaux, B 23, 554) Light-yellow needles, sl sol alcohol and benzene

Reactions -1 Silver nitrate converts it into (NMe₂ C₆H₄)₂O -2 On heating with reduced

copper (10 pts) at 300° it yields NPhMe Salts—B"H₂Cl₂ [176°] White mass becoming coloured in the air, extremely sol water - B"H, PtCl, 2aq - B"H, FeCy, 6aq white owder, m sol water -B"C, H₂(NO₂), OH powder, m sol water — B"C₆H₂(NO₂)₃OH [142°] Yellow needles (from hot alcohol) — B"2C,H₂(NO₂₎₂OH Amorphous [146°] — B'HNCS [168°], pearly plates Tetra-methyl-di-amido di-phenyl di-sulphide

 $(NMe_2C_6H_4)_2S_2$ Di sulphido- or di thio di [118°] Formed by adding methyl anılıne S₂Cl₂, diluted with petroleum ether, to a dilute solution of dimethylaniline in the same solvent (Merz a Weith, B 19, 1570) Formed also by heating di methyl p amido phenyl ethyl di thio carbonate with an alcoholic solution of aniline at 200° (Leuckart, J pr [2] 41, 208) Small yellow needles, e sol CS_2 , more sparingly in hot benzene, alcohol, and petroleum ether, nearly insol water Copper powder removes the sulphur at c 230° forming dimethylaniline and other products By the action of Fe₂Cl₆, or of alcoholic NH, and silver nitrate, it is con verted into tetra methyl di amido di phenyl di oxide (NMe₂C₆H₄)₂O₂ By tin and HCl, or by sodium amalgam, it is reduced to di methylamido phenyl mercaptan, which is readily reoxidised to the di sulphide Its salts are gummy and amorphous, they are decomposed by water

Tetra-methyl-tetra-amido-di phenyl-disulphide (NMe₂C₆H₃(NH₂))₂S₂ Formed by atmo spheric oxidation from di methyl-di-amido phenyl mercaptan NMe₂C₆H₃(NH₂)SH (Bernthsen, A 251, 1) Thick oil, sol ether, alcohol, and benzene Dissolves in acids, but reppt by alkalis In benzene solution it combines with sulphur forming a persulphide [97°], apparently

C₂₂H₄₄N₄S₃ DI-METHYL AMIDO-DI-PHENYL PHONE C.H. SO.O.H. NMe. [78°] (R), [82°) (M a M) Formed by heating dimethyla niline with benzene sulphonic chloride (Michler, B 10. Phenol-blue. Formed by adding quinone chlor
N. C.H., NMe. 1742, Van Romburgh, R. T. C. 2, 305, Michler a. Meyer, B. 12, 1791, Hassencamp, B. 1275) Needles (from alcohol), insol water, ve sol alcohol, ether, and benzene HClAq at 180° splits it up into MeCl, aniline, and benzene Zinc and H₂SO₄ reduce it to phenyl mercaptan and dimethylaniline HNO₂ gives yellow crystals of tetra nitro-methyl aniline [127°]

METHYL-AMIDO-PHENYL-THIAZOLE

 $C_{10}H_{10}N_2S$ to S-C(NHMe) N [138°] From CH CPh

w bromo acetophenore and methyl thio urea (Traumann, A 249, 46) Yellow plates (from ether), insol water, m sol alcohol With HClAq at 220° it yields methylamine

TETRA METHYL DI AMIDO-D' PHENYL-

THIENYL METHANE C₂₁H₂₄N₂S 1 e (NMe₂ C₆H₄)₂CH C₄H₄S Throphene leuco-mala-chite green [98°] Formed by heating thiophenic aldehyde with dimethylaniline, ZnCl. and a little alcohol (Peter, B 18, 538, Levi, B Formed also by heating dimethyl ani-20, 514) line with thienyl glyoxylic acid C,H,S CO CO2H and ZnCl₂ (P) Needles, insol water, v sol alcohol and ether The alcoholic solution turns green in the air MnO2 and dilute H2SO4 oxidise it to the carbinol (NMe, C,H,),C(OH) C,H,S, which is a dark brown oil, sol alcohol and ether, and forming salts which dye a splendid yel-Throphene green -Platino-C₂₁H₂₁N₂SH₂PtCl - Picrate $(Th \iota o p h \cdot n e$ lowish green chloride C, H₂₄N S2C₆H₂(NO₂₎₃(OH) [c 208°] Yellowish green needles, sl sol cold water, v sol alcohol

Dr methylo dr rodide C,H₃S CH(C₆H₄ NMe₃I)₂ [212°] White plates

TETRA METHYL-DI-AMIDO DI-PHENYL-THIOKETONE v Tetra methyl di amido-thio Benzophenone

DI-METHYL DI AMIDO PHENYL THIO-SULPHURIC ACID NMe₂ C₂H₃(NH₂)S SO₃H [193°-204°] Obtained by adding an alkali to a $\frac{1}{15}$ p c solution of methylene red until the colour is destroyed, then acidulating with HOAc and exposing to the air Formed also by the action of a strong solution of SO₂ on di methyl di amido phenyl mercaptan (Bernthsen, A 251, 1) Crystals, sl sol water and alcohol Its dilute aqueous solution gives a purple colour with traces of iodine oi of FeCl₃ The hydrochloride crystallises in prisms

Reactions —1 A mixture of di methyl di amido phenyl thio sulphuric acid with dimethyl aniline when oxidised by k,Cr,O, and HOAc NC₆H₃(NMe₂)

forms the indamine C₄H₄ | S, an NMe₂ O SO₂ | S, an emerald green powder (containing ½aq), and yields NMe₂ C₄H₄ NH C₄H₃(NMe₂) S SO₃H on reduction, a body which is v sol hot alcohol and acids —2 A mixture of the thio-sulphuric acid

with aniline hydrochloride gives on oxidation

C₁₄H₁₅N₂S₂O₂ to C₄H₄(N₁Me₂)

NH₂ O SO₂

S (?) an

insoluble green compound decomposed by water Prolonged boiling with dilute FeCl, gives N(NMe2)

S, a blue powder with bronze

iustre —8 A mixture of di-methyl-di amidophenyl thiosulphuric soid with o-toluidine yields

C.H.

on oxidation the homologous C₁₃H₁, N₂S₂O₃ as a bluish grey powder

Tetra-methyl-di amido phenyl thiosulphuris acid C₆H₄(NMe₂)₂S SO₂H [175°-182°] Obtained by dissolving tetra methyl p phenylene diamine (27g) in HCl (156 c,c of 38 p c) and adding aluminium sulphate (10g), and sodium thiosulphate (6 6 g) dissolved in water (36 c c) A cold solution of K,Cr,O, (25 c o of a 6 67 p c solution) is then added, and the resulting liquid left to stand The precipitate which then separates is recrystallised from alcohol (Bernthsen, A 251, 60) Plates, sol hot water and acids Zinc and HCl reduce it to the mercaptan C₆H₄(NMe)₂SH

TETRA-METHYL DI p-AMIDO-DI-PHENYL THIO UREA C. H., N.S. t.s. (NMe, C.H., NH), S [186°] Formed by boiling di methyl-p phenylene diamine with alcoholic CS₂ (Baur, B 12, 533) White needles, insol water and cold alcohol—B"H,Cl, crystalline powder

Acetyl derivative [71°] White plates TETRA - METHYL-DI-AMIDO-DI-&-PHE.

NYL-TOLUIC ALDEHYDE C₂H₂N₂O te (NMe₂·C₄H₃)₂CH C₂H, CHO Aldehyde of the leuco base of malachite green [143°] Obtained by boiling an alcoholic solution of terephthalic aldehyde C₄H₄(CHO), with di methyl anline and ZnCl₂ (W Löw, A 231, 381) Prismatic needles (from chloroform) Forms a crystalline compound with NaHSO, Its phenyl hydrazide melts at 225°—B"H₂PtCl₅

TRI METHYL-TRI AMIDO-DI-PHENYL-TOLYL CARBINOL C₂H₂,N₃O Formed by heating rosaniline chloride (1 pt) with MeI (2 pts), NeOH (8 pts), and KOH (1 pt) (Hofmann) Formed also by allowing an alcoholic solution containing rosaniline and 'iodine green' to stand in the cold (Girard a Willm, Bl [2] 25, 200) The salt NHMe C₄H₃Me C₄C₆H₄NHMeCl is one

of the substances known as Hofmann's violet (Hofmann, C R 54, 428, 56, 945, 1033, 57, 1131) Its absorption spectrum has been studied by Hartley (C J 51, 172)

Penta-methyl-tri-amido di-phenyl-tolyicarbinol

NMe₂·C₆H₃Me C(OH)(C₆H₄NMe₂)(C₆H₄NMeH)
The obloride NMe₂ C₆H₃Me C
C₆H₄NMe₂
C₇H₄NHeCl

is probably the chief constituent of Hofmann's violet obtained by heating rosaniline with McCl It has a green lustre and forms a violet solution in water. The solution is decolourised by zine dust. HCl turns the solution first green, then yellow. NaOH gives a brownish-red pp. Conc. H₂SO₄ gives a brownish-yellow solution changed, on dilution, through green to blue. It dyes wool, silk, and mordanted cotton violet.

Hexa-methyl-tri-amido-di-phenyl-tolyl carbinol $\text{NM}_0(C_dH_d\text{Me} \in C(OH)(C_dH_d\text{NM}e_d)_s$. The zinc double salt of the methylo chloride of this body C_dH_d , N_dCl_d or

NMe₂ C_cH₄Me C C_cH₄NMe₃Cl appears to

constitute the dye known as 'iodine green,' which is obtained by heating rosaniline with McCl, or by the action of McCl on Hofmann's violet. The

7 Z

scrresponding iodide $C_{ir}H_{35}N_{1}I_{2}$ aq is obtained by beating MeI (2 pts) with MeOH (2 pts) and resamiline (1 pt) at 100° (Hofmanna Gurard, B 2, 440) The zinc double chloride forms a bluishgreen aqueous solution, turned reddish yellow by hydrochloric acid, and rendered colourless by caustic soda. It dyes silk green. When heated strongly in the dry state it becomes violet. Its absorption-spectrum has been studied by Hartley (C J 51, 175). Iodine green may be reduced to penta methyl tri amido-di phenyl tolyl methane. NMe₂ ($c_{1}H_{1}$ Me CH($c_{2}H_{1}$ Me) (173°) (O. Fischer a. G. Körner, B. 16, 2910). Besides the bodies here described other methylated rosamilines are doubtless formed in the methylation of rosamiline.

DI - METHYL - AMIDO - PHENYL p-TOLYL SULPHONE C₁₅H₁₇NSO₂ 2 e

[4 1]C_sH₄Me SÖ₂ C

GH₄Me SO₂Cl and dimethylaniline (Michler a Meyer, B 12, 1793) Split up by HCl at 180° into MeCl, aniline, H₂SO₄, and toluene Zinc and H₂SO₄ reduce it to p tolyl mercaptan and dimethylaniline

DI-METHYL-p-AMIDO-PHENYL-UREA C₅H₁₃N₅O ie NH₂CO NH C₆H₄NMe. [179°] From potassum cyanate and di methyl-p-phenyl ene-diamine (Binder, B 12,536) Long needles, sol hot water—R'H-PtCl. vallow leaflets

ene-diamine (Binder, B 12,536) Long needles, sol hot water — $B'_2H_2PtCl_s$ yellow leaflets Tetra-methyl-di p amido-di-phenyl-urea (P,H₂N₄O *e CO(NH C_sH₄NMe_s)₂. [262°] (B), [246°] (M a Z) Obtained by heating urea with di-methyl p phenylene diamine (Binder, B 12,585) The same body is apparently obtained by the action of COCl₂ on di methyl p phenylene diamine (Michler a Zimmermann, B 14, 2179) — $B''H_2Cl_2$ soluble crystalline powder — $B''H_2SO_4$ sl sol water — $B''H_2PtCl_6$

METHYL AMIDO PROPANE SULPHONIC ACID NHMe CH, CHMe SO, Η [220°-223°] From methyl propylene ψ-thio-urea and brominewater (Gabriel, B 22, 2989) Colourless columns, γ e sol water

METHYL a-AMIDO-PROPIONIC ACID

C₄H_eNO₂ 2.6 CH₂ CH(NHMe) CO₂H [260°] From a chloro proponic ether and aqueous methylamine at 130° (Lindenburg, J pr [2] 12, 244) Prisms Decomposed on fusion Tastes sweet Its copper salt crystallises in dark blue prisms—HA'HCl [110°] Deliquescent prisms HA'HCl₃ Trichine prisms—HA'HNO₃ [126°] Monoclinic prisms

Di-methyl a-amido-propionic acid Methylo chloride CH, CH(NMa,Cl) CO,H Formed by treating a-chloro propionic ether with trimethylamine, saponifying the resulting ether with baryta, and adding HCl (Brühl, B 9, 34) Very hygroscopic, forming (C₄H₄NO₂Cl)₂PtCl₄ crystallising in roseate prisms, and C₄H₄NO₂AuCl₄ crystallising in golden needles The corresponding Anhydride of the Methylo-hydroxide

OH₂ CH CO NMe₂ O or 'betaine' is formed on adding baryta to the methylo-chloride and subsequently neutralising with H₂SO₄. It forms extremely deliquescent crystals, and is neutral in reaction. The loade (C₂H₁₂NO₂)₂HI forms long colourless prisms, v sol alcohol and hot water

DI-METHYL AMIDO PROPYL ALCOHOL v. Dr-methyl oxy-propyl amine

Tetra-methyl-s-di-amido-usopropyl alcohel C,H₁₈N₂O ve (NMe_xCH₂)_zCH OH (170°-185°). Formed from di-chloro-usopropyl alcohol (s di-chlorhydrın) and NMe_zH at 60° (Berend, B 17, 510) Liquid, v e sol water—B'H₂PtCl_e: yellow plates

Benzoyl derivative (NMe, CH₂)₂CH OBL. Forms a platino chloride B"H₂PtCl₂ crystallising in tables

DI-METHYL-AMIDO-PROPYLENE GLYCOL C₅H₁₃NO₂ e NMe₂ CH₂ CH(OH) CH₂OH (217°) From dimethylamine and chloro propylene glycol (chlorhydrin) (Roth, B 15, 1153) Thick syrup, v e sol water, alcohol, and ether—B'₂H₂PtOl₆

Methylo-chloride

NMe, Cl CH₂ CH(OH) CH₂(OH) From the chlor hydrin and NMe, at 100° (V Meyer, B 2, 186, Hannot, A Ch [5] 17, 99) Needles, v e sol water—(C₂H₁₈NO₂Cl)₂PtCl₄ crystalline tables—C₂H₁₈NO₂AuCl₄ [190°] Orange crystals, m sol alcohol

Dr-benzoyl dervative
NMe₂ CH₂ CH(OBz) CH₂ (OBz) oil — Picrate
B'C₆H₂ (NO₂)₄OH [100°] Laminæ (Roth, B
15. 1158)

DI-METHYL-(B 2)-AMIDO-QUINOLINE

NMe₂C CH C CH CH

C₂H₄(NMe₂)N 16 | | | [56°]

CH CH C N CH C (C), [58°] (O) (c 335°) Prepared by boiling a mixture of u-di methyl p phenylene diamine (25 pts), glycerine (60 pts), nitro-benzene (15 pts), and H₂SO₄ (50 pts) (La Coste, B 16, 672) Colourless crystals V sol alcohol, ether, and benzene

Picrate B'(C₆H₂(NO₂)₃OH) very fine orange needles [215°]

Methylo rodide B'MeI long red needles —(BMeCl)₂PtCl₄

Methylo-chloride B'MeClaq [244°]
Long scarlet hygroscopic needles (Ostermayer,
B 18, 596)

Methylo chloride of the tetrahydride NMe, C₃H₁₀NMeCl aq [220°], fine colourless needles With IClitforms NMe C₄H₁₀NMeClICl [127°], separating in small yellow crystals (Ostermayer, B 18, 596)

TETRA - METHYL - DI - AMIDO - QUINONE C_sH₂(NMe₂)₂O₂ [174°] Red tables Formed by dissolving ordinary quinone in aqueous dimethyl amine (Mylius, B 18, 467)

DI-METHYL-AMIDO-SULPHO-BENZOIC ACID C₆H₄(NMe₂)(SO₃H) CO₂H [4 2 1] Obtained by heating the silver salt of amido sulpho benzoic acid with MeI and MeOH at 100° (Hedrick, Am 9, 413) Easily soluble crystals—CaA"—BaEtA".

TETRA-METHYL-DI-AMIDO-THIOBENZO-PHENONE C, H₂N, Ste CS(C, H₁NMe₂)₂ [194°] (B), [202°] (G) S (alcohol) 072 at 18° S (ether) 27 at 18° S (chloroform) 458 at 18° Formed by passing H₂S into an alcoholic solution of the hydrochloride of tetra methyl diamido benzophenone imide (auramine) at 60° (Fehrmann, B 20, 2857, Baither, B 20, 1731, 3289) Formed also by the action of CS₂ on auramine (Graebe, B 20, 3266) Obtained also from CSCl₂ and dimethylaniline Ruby red crystals, with blue lustre Insol water and light petroleum, sl sol other solvents Its

solutions in benzene and CS, are dark red with green fluorescence

Reactions -1 Hot dilute hydrochloric acid gives H2S and tetra-methyl di amido benzophenone - 2 Water at 120° under pressure also forms CO(C₆H₄NMe₂)₂.—8 Boiling concentrated mitric acid forms CO(C₆H₂(NO₂)₂.NMe NO₂)₂, whence hydroxylamine hydrochloride forms $CO(C_cH_2(NO_2)_2 NMeH)_2$ [c 196°] —4 By heating with excess of benzyl chloride it is converted into COl₂(C₄H₄, NMe₂)₂, a greyish green powder, decomposed by writer with production of CO(C.H.NMe.). - 5 Aniline hydrochloride at 150° forms phenyl auramine NPh C(C₆H₄NMe₂)₂ [171°] — 6 Phenyl-hydrazine at 100° forms CO(C₆H₄ NMe₂)₂ Aniline at 150° also forms this ketone —7 Hydroxylamine gives the oxim of tetra methyl di amido benzophenone -8 Dis tillation over red hot zinc dust yields di methyl aniline and tetra methyl-di amido di phenyl methane -9 Acetyl chloride in the CS, solution forms C17H20N2SAcCl, which forms a red alco holic solution and a greenish yellow solution in benzene It begins to decompose at 160° -10 Benzoyl chloride in CS₂ forms a similar compound C_{1,}H₂N₂SBzCl, which is insol water, but decomposed by solution in alcohol— Boiling with Ac2O and NaOAc forms $C_{38}H_{46}N_4SO_4$, a dark grey powder -12 Methyl wolvde appears to give $C_{17}H_{28}N_2SMeI$, which forms green plates with coppery lustre, decom poses at 108°, and yields a deep bluish green aqueous solution with red fluorescence It dyes silk green -13 CSCl₂ acting on its CS₂ solution forms a black powder, probably C1,7H20N2SCSCl2. In chloroform solution, CSCl2 forms white crusts of CCl₂(C₆H₄NMe₂)₂CHCl

METHYL-AMIDO-THYMOQUINONE

C₁₁H₁₈NO₂ 1 e C₃H, C₆HMe(NHMe)O₂ [74°] From methylamine and thymoquinone in alcoholic solution (Zincke, B 14, 97) Dark violet laminæ (from very dilute alcohol) Volatile with steam M sol water, v e sol alcohol The solutions are deep violet Alcoholic HCl converts it into methylamine and oxythymo

D: methyl amido thymoquinone C₁₂H, NO₂ te C3H, C6HMe(NMe2)O2 Prepared by mixing dimethylamine with thymoquinone in alcoholic solution (Schulz, B 16, 899) Dark coloured Volatile with steam Split up by heating with dilute HCl into oxythymoguinone and di

methylamine

Di methyl di-amido-thymoquinone $C_{12}H_{18}N_2O_2$ is C_3H_7 , $C_6Me(NHMe)_2O_2$ Formed, together with methyl amido thymo quinone, by treating a cold concentrated alcoholic solution of thymoquinone with methylamine (Zincke) Formed also by the action of methylamine on di bromo thymoquinone Long reddish violet needles (from alcohol) Decomposed by KOH or H₂SO₄ in alcoholic solution into methylamine and di oxy thymoquinone

METHYL-AMIDO-TOLURNE

TOLUIDINE

Methyl-di-amido-toluene v. METHYL-TOLYL-ENE DIAMINE

Methyl-tri-amido-toluene C,H,,N, C,H2Me(NH2)3(NHMe) The hydrochloride B"H,Cl, aq is prepared by reducing the nitramine of di-nitro-methyl-o-toluidine with tin and

HCl (Van Romburgh, R T C 3, 400) It forms small crystals

Di-methyl-amido-toluene sulphonic acid C₀H_{1,1}NSO, te NMe₂C₀H₃Me SO₃H [2 1 4?]. Formed by heating di methyl-o toluidine (1 pt) with H₂SO₄ (4 pts) at 180° to 210° (Michler a. Sampaio, B 14, 2168) Large glittering prisms (from water), insol alcohol, v sol hot water -CaA'₂ (dried at 130°) Nodules —BaA'₂ (dried at 130°) Laminæ, v sol hot water — ZnA'₃ needles

TETRA METHYL-DI AMIDO-DITOLYL NMe₂ C₄H₃Me C₄H₃Me NMe₂ Tetra - methyl-tolidine [80°] Formed by oxidising di methyl-o toluidine with MnO₂ and dilute H₂SO₄ Tetra - methyl-Formed also by methylation of di amido ditolyl (Michler a Sampaio, B 14, 2170) White plates, sol ether and hot alcohol, insol water -B"H2Cl2 white needles -B"H2PtCl2 yellow

crystalline pp

Tetra methyl di amido-ditolyl C18H24N2 1 e N Me₂ C.H. Me C.H. Me NMe₂ [190°] Formed in small quantity by heating dimethyl o-toluidine with H₂SO₄ (M a S) Long needles, sol hot alcohol, ligroin, and ether, insol water Gives a green colouration with Fe, Cl, and yellow colour with CrO,

Tetra-methyl-di-amido-ditolyl (?) $C_{18}H_{24}N_2$ 2.e $NMe_2 \cdot C_6H_3Me \cdot C_8H_3Me \cdot NMe_2 = [57^{\circ}]$ Prepared by heating dimethyl p toluidine with H.SO. (Michler a Pattinson, B 14, 2167) White needles, sol alcohol and ether, insol water

-B"H,Cl,PtCl

DI - METHYL - AMIDO - TOLYL - BUTANE C₁₃H₂₁N 1e C₄H₄, C₆H₄Me NMe₂ [251°] From amido tolyl butane and MeI (Effront, B 17, 2339) —B .H2PtCl.

DI - METHYL AMIDO - TOLYL METHYL KETONE C,,H,,NO 1 e $[1\ 2\ 5]C_6H_3(CH_3)(NMe_2)$ CO CH_2 [95°] yellowish prisms, e sol alcohol, ether, and hot water, nearly insol petroleum ether by methylation of amido tolyl methyl ketone

(Klingel, B 18, 2699) METHYL a AMIDO n VALERIC ACID

C.H.,NO₂ ie CH, CH, CH, CH, CH(NHMe) CO H Obtained by heating butyric aldehyde with conc aqueous HCy, adding methylamine, and heating The nitrile then separates as an oil, which is hydrolysed by prolonged boiling with dilute HClAq (Menozzi a Belloni, G 17, 116) Long glistening needles (containing aq), decom posed partially at 110° with formation of a sublımate

Salts -CuA'22aq blue prisms -HA'HNO2. prisms, v sol water

Methyl a-amido isovaleric acid C.HisNO. s.s (CH₂)₂CH CH(NHMe) CO₂H Formed by boiling a bromo isovaleric acid with aqueous methylamine (Duvillier, C R 88, 425, A Ch [5] 21 434) White crystalline powder, v e sol water, m sol hot alcohol, insol ether Neutral in reaction With cyanamide it forms a creatinin C.H., N.O. crystallising in slender needles, v. sol bouing alcohol (Duvillier, C R 95, 456) — HA'HOI Crystallises with difficulty H,A',H,SO, HA'HAuCl, aq v sol water prisms , short trimetric prisms copper salt forms an intense blue solution

Di - methyl - a - amido - isovaleric Methylo-rodide of the methyl ether. Pr CH(NMe,I) CO,Me. Formed by heating MeI

4 pts) with zinc amido-valerate (1 pt) and ZnO (1 pt) at 110° for 16 hrs (Duvilher, C R 110, 640) Yields {Pr CH(NMe₂Cl) CO₂H₂.PtCl₄4aq and Pr.CH(NMe₂Cl) CO₂H₃.PtCl₄4aq and Pr.CH(NMe₂Cl) CO₂HAUCl₂ METHYLAMINE ONH₅ 4c CH₅ NH₇ Mol w 31 (-6°) (Hofmann, B 22, 701) S G -108 ·699 H F p 9,540 H F v 8,880 (Thomsen, Th) H C 256,900 (Müller, Bl [2] 44,609) Heat of neutralisation by HCl · 25,900 (Müller, A Ch (5116,531) S (cas) 1150 at 125° . 950 at 25° [6] 15, 531) S (gas) 1150 at 125°, 950 at 25°

Occurrence -1 In bone oil (Anderson, A 80, 44) -2 In Mercurialis annua and M perennas (Schmidt, B 10, 2226, A 193, 73, cf Reichardt, Z 1868, 734) —3 In herring brine (Bocklisch, B 18, 1922) —4 In crude wood spirit (G Williams, Chem Gaz 1853, 409, Commaille, J 1873, 686, Vincent, C R 77, 898) —5 In the product of the distillation of beet root molasses (Duvillier a Buisine, A Ch [5] 23, 317)—6 In the 'yolk' or 'sumt' of sheep When an aqueous extract of this substance is allowed to stand for some time, and is then boiled, it gives off 4 pts of NH₂Me for 95 pts of NH, and 1 pt of NMe, (Buisine,

C R 104, 1292) Formation -1 Discovered by Wurtz, who obtained it by distilling methyl cyanate (or cyanurate) with potash (C R 28, 223, 323, area with potash (Wurtz) —3 In small quantity, together with NHMe₂ and NMe₃, by heating ammonia with MeI (Hofmann, A. 79, 19) Formed also by heating the methyl ethers of other morganic acids with ammonia -4 By heating wood spirit with ammonium chloride or iodide at 800° (Berthelot, J 1852, 551, Girard, Bl [2] 24, 121, cf Weith, B 8, 458) By heat ing methyl alcohol (3 pts) with NH Cl (2 pts) and HCl (1 pt) at 207° for 30 hours Dusart a Bardy converted one third of the NH₃ into NH₂Me (C R 74, 188).—5 By heating methyl alcohol with ammoniacal ZnCl₂ (Gasiorowsky, B 17,639) —6 By heating morphine or codeine with KOH (Wertheim, A 73, 210, Anderson, A 77, 874)—7 By distilling glycocoll with BaO (Cahours, A 109, 28)—8 By the action of chlorine on theobromine or caffeine (Rochleder a Hlasiwetz, J 1850, 434, 437) -9 In small quantity by reducing HCy with zinc and dilute H₂SO₄ (Mendius, A 121, 129) —10 By passing a mixture of HCy and hydrogen over platinum-black at 110° (Debus, A 128, 200) —11 By re ducing nitro methane with iron filings and dilute HOAc (Preibisch, J pr [2] 7, 480)—12 By digesting di methyl unc soid with HClAq for several hours at 170° (Hill a Mabery, Am 2,

Preparation -1 By distilling methyl cyanurate with aqueous KOH (Wurtz) The distillate is received in dilute HCl, and the methylamine hydrochloride dried and distilled with quicklime solution of methyl-bromo-amide thus obtained is then run in a slow stream into a 30 p c solution of 8 mols of KOH heated to 60°-70° and digested for 10 or 15 mins till decolourised. The solution is then boiled and the methylamine received in HCl, the yield is 87 pc of the theoretical (Hofmann, B. 15, 765, 18, 2741).—

3 Methyl nitrate (1 mol) is heated in closed vessels at 100° with a solution of ammonia (1 mol) in wood spirit Besides the nitrate of mono methyl-amine there is formed tetra methyl ammonium nitrate together with small quantities of di- and tri methylamine nitrates At the end of the reaction the product is neutralised with sulphuric acid, heated to evaporate off the alcohol, and the residue decomposed by potash, and the bases received in hydrochloric acid The hydrochlorides are treated with absolute alcohol to remove the ammonium chloride, and again decomposed, the bases being received in sulphuric acid The sulphates are then treated with absolute alcohol in which mono methyl amine sulphate is insoluble To remove the last traces of impurities the insoluble sulphate is again decomposed and converted into di methyl oxamide, which yields on decomposition pure mono-methyl amine (Duvillier a Buisine, A Ch. [5] 28, 322, cf Juncadella, C R 48, 342) -4 By the action of tin and HCl on chloropierin (Wallach, A 184, 51, cf Geisse, A 109, 282) 5 By heating dry ammonium methyl sulphate at 300° and distilling the product with potash (Milner Morrison, Pr = E = 10, 275)

Properties —Colourless gas with strong am monacal odour Not solid at -75° Turns red litmus blue Fumes strongly with HCl Rapidly absorbed by water and by charcoal Of all known gases it is the most soluble in water Burns in air with livid yellowish flame (differ ence from NH_a) The aqueous solution of methylamine is extremely caustic, and gives off the gas when boiled It ppts metallic salts, for the most part in the same manner as ammonia Zinc hydroxide is, however, soluble in a large excess of methylamine With cupric salts it gives a bluish-white pp dissolving in excess and forming a deep blue solution With salts of Cd, Ni, and Co it forms pps insoluble in excess (difference from NH₂) It ppts lead nitrate but not lead acetate With mercurous nitrate it gives a black pp, with HgCl₂ a white pp, with AgNO₂ it gives a pp of Ag₂O soluble in excess It dissolves AgCl With chloride of gold it gives a brownish yellow pp , soluble in excess Platinic

chloride gives a yellow crystalline pp

Reactions -1 Passage through a red-hot tube converts it into hydrogen, CH4, ammonia, and HCy No acetylene, benzene, or C₂H₄ is formed (Muller, Bl [2] 45, 438) When an aqueous solution of methylamine is set on fire, HCy is found in the residue (Tollens, Z [2] 2, 516) —2 Heated potassium forms hydrogen and KCy —3 Cyanogen chloride forms methyl cyanamide (Cahours a Cloez, C R 38, 354)—4

Iodine forms MeNI₂—5 CO₂ forms methylamine
methyl-carbamate—6 According to Berthelot, heating with saturated HIAq yields ammonia and CH₄—7 COCl₂ yields NHMe COCl [90°]—8 Liquid McCl, under pressure, forms NMe₄Cl and NMeH,Cl (Vincent a Chappuis, C R 102, 436) -9 MeBr (1 mol) in MeOH at 100° forms, chiefly, NMe,Br In like manner MeI forms NMe,I (Duvillier a Buisine, C R 90, 1426) — 10 Benzore aldehyde added to aqueous NMeH, forms PhOH NMe, an oil (c 180°) which yields bensyl-methylamine (185°) on reduction (Zaunschirm, A 245, 281).—11 o-Oxy benzoic alde-hyde forms C.H.NO (229°) (Dennstedt a Zimmermann, B 21, 1553) -12 'Dicyanamidobenzoyl' (cf vol 1 p 155) forms small needles of $C_{16}H_{16}N_4O$ (Griess, B 18, 2420) —13 Diazobenzene chloride added to a cool 33 p c solution of methylamine forms MeN(N2Ph)2 [113°] which crystallises in yellow needles, v sol. ether, m sol alcohol It is reduced by Zn and HOAc to Boiling methylamine and phenylhydrazine dilute H2SO4 gives nitrogen, aniline, MeOH, phenol, and some PhN₂C₆H₁NH₂ (Goldschmidt a Badl, B 22, 934) — 14 o Diazo-anisole chloride forms yellow needles of the compound MeN(N₂ C₂H₄OMe)₂ [141°] (G a B) —15 p Dt-azo ansole chloride forms MeN(N₂C₃H₄OMe)₂ [112°] (G a B) —16 p-Diazo-toluene chloride forms MeN(N₂C₃H₄Me)₂ [147°] Salts —B'HCl Large delique reent lamins

(from water), may be sublimed Sol alcohol, in sol CHCl, —B'HAuCl, aq Trimetric crystals (Topsoe, J 1883, 618) —B'HAuCl, Monoclinic (T) — B'₂H₂PtCl₂ Golden hexagonal (Ludecke, J 1880, 511) S 2 at 14° Golden hexagonal scales alcohol, not decomposed by boiling water (De Connex, Bl [2] 45, 131)—B',H,Cl,Ptbr, Scarlet crystals (Maly a Hinterberger, M 3, 89)—
B',PtCl, Insoluble green powder—B',PtCl,
V e sol water—B',H,Tcl, Small hexagonal brownish black plates (Vincent, Bl [2] 43, 154) B'₁H₁Rh₂Cl₁ (Vincent, C R 101, 322)—
B'₂H₂H₃Cl₂ Monoclinic crystals, v sol water
—B'HHgOl₂ Rhombohedral crystals (T)—
B'₂H₂CuCl₄ Trimetric crystals —B'₂H₂PdCl₄— B'HBr Large deliquescent plates (from alcohol), v sol water and alcohol—B'HI—B'₄H₄I₃BiI₄. Scarlet pp (Kraut, A 210, 312)—B'₄H₃I₂BiI₄. Crystalline pp (K)—B'HNO₃ Elongated tri metric prisms Deliquescent, v sol water, al sol cold alcohol [100°] (Franchimont, R T C 2, 338) -B',H,SO, Deliquescent needles, insol 2, 365) — B. H. SO. Deliquescent accure, moral alcohol — B'HMeSO. Crystals, v e sol water (Claesson a Lundvall, B 13, 1701) — B'HVO, (Bailey, C J 45, 692) — B'HVO, (aq Colourless accoular crystals (Ditte, C R 104, 1844) — B', (H, O)(V, O), (aq Yellow powder (D)) $B'_{2}(H_{2}O)(V_{2}O_{3})_{2}$ 4aq $B_{4}(H_{2}O)_{2}(V_{2}O_{3})_{3}$ 3aq (B) $-B_{2}H_{2}CO_{3}$ Formed, together with methyl carbamic acid NMeH CO2H, by decomposing CaCO, with methylamine hydrochloride Deposited in crystals from the liquid distillate - B.H C.O. Prisms, v sol water, insol alcohol -Benzene sulphonate [147°] (Norton a Westenhoff, Am 10, 129) -Valerate [81°] NH₂Me2CMe₂CO₂H? (175°) NH, Me and tri methyl-acetic acid at 150° (Franchimont a Klobbie, R T C 6, 234)

Acetyl derivative C, H, NO 16 NMeAcH Methyl acetamide [28°]. (206°) From EtOAc and aqueous methylamine at 150° (Hofmann, B14, 2725) — NMeAcHHNO, [58°] Large hygroscopic crystals (Franchimont, R T C 2,

341)

Dr acetyl derivative C,H,NO, as NMeAc₂. (192°) A product of the action of Ac₂O on methyl-acetyl urea (H.) Liquid, miscible with water Split up by HCl into methylamine and acetic acid

Tri-chloro-acetyl derivative
CCl, CO NHMe [106°] From CCl, CO, Et and aqueous methylamine (Franchimont a Klobbie, R T C 6, 234) White crystals, sl sol. water and other Slowly attacked by pure HNO., which gives off N.O

derivative CMe, CO Mills Trom Me, C COCI Valeryl [91°] (204°) and NH₂Me and NH, Me Methylamine and Me₂C CO₂Me yield only (Me₂C CO₂H), NH, Me V sol water and alcohol (F a. K.) Pure HNO₂ gives off

C.H.; CO NHMe Thick liquid (F Heptoyl (266°) derivative 8 G 15 895 aK)

Bensoyl C.H. CO NHMe derivative Crystallises from alcohol (Romburgh, R T C 1, 388)

o Amido benzoyl derivative

C₆H₄(NH₂) CO NHMe [80°] From isatoic acid and methylamine solution (Weddige, J pr [2] 86, 150) Thick prisms (from benzene), v e sol alcohol and ether, sol hot water Ac₂O gives C₆H₄(NHAc) CO NHMe [172°] BzCl forms $C_6H_4(NHBz)$ CO NHMe [181°] (Körner, J pr [2] 36, 159)

Other alkoyl derivatives are described under the acids from which they are derived

Methyl-di chloro-amine CH, NCl, (60° un Pungent yellow liquid (Köhler, B 12, cor) 770)

Methyl-di-bromo-amine CH, NBr, Formed by the action of bromine and potash on methyl amine hydrochloride (Hofmann, B 15, 767) Extremely pungent liquid Slowly converted into methylamine by HCl

Methyl-di 10do-amine CH, NL, Formed by the action of iodine on aqueous methylamine (Wurtz, A Ch [3] 30, 455) Prepared by adding iodine (1g) and water (50g) to methylamine hydrochloride, and then adding aqueous NaOH (Raschig, A 230, 221) Brownish red pp , quickly becoming brick red Completely soluble in aqueous HCl, soon decomposing into methylamine and ICl Ammonia forms NMeH₂ and NHI₂ Cold potash dissolves it, forming methylamine, KIO₂, and KI

Methyl nitro-amine CH, NH NO2. Obtained by treating methyl chloroformate with methylamine, nitrating the resulting methyl methyl-carbamate CH,NH CO OMe, and boiling the product with ammonia (Franchimont a Klobbie, R T C 7, 354, 8, 297) Formed also by decomposing NO2 NMe CO CO NMe NO2 with aqueous ammonia Colourless needles, sol alco hol Strongly acid in reaction Converted by KOH and MeI into crystalline Me.N NO. KMeN NO. Slender needles, sol alcohol and

Dimethylamine C₂H₇N s.e (CH₃)₂NH Mol w 45 (7 2°) (Hofmann, B 22, 702) 687 S V 152 4 (Ramsay) H F p 12,720 (Thomsen), 3,500 (Muller, Bl [2] 44,609) H F v 10,980 (Thomsen, Th) HC 42,600 (M) Heat of neutralisation (by HCl) 23,980 (Müller, A Ch [6] 15, 531)

Occurrence —In herring-brine (Bocklisch, B 18, 1924)

Formation -1 One of the products of the action of MeI on ammonia (Hofmann) -2 A mixture of mono, di-, and tri methyl amine is obtained by heating methyl alcohol with ammoniacal ZnCl, at 200°-220° (Merz a Gasiorowski, B 17, 639) -3 In small quantity by heating the sulphite of aldehyde ammonia in a sealed tube, or by distilling it with lime (Petersen, 4. 102, 317)

Preparation —1 The mixture of iodides obtained by heating ammonia with MeI is distilled with potash, and the evolved bases dried by KOH and condensed by a freezing mixture, the bases NMe₂, NMe₂H, and NMeH₂ being separated by means of oxalic ether (Hofmann, Pr 12, 380) —2 The bases obtained from MeBr and NH, are treated with introus acid, and the dimethylintrosamine decomposed by HCl and distilled over sodium (Hofmann) —8 Nitroso-dimethylianline hydrochloride (2pts) is boiled with water (90 pts) and aqueous NaOH (10 pts of S G 125) (Baeyer a Caro, B 7, 964, 8, 616)

Properties—Highly alkaline liquid or gas Has not been solidified. If to an alcoholic solution of the base picryl chloride $C_0H_2(NO_2)_3Cl$ be added, and then H_2SO_4 followed by water, there is formed a characteristic yellow pp of tri nitrodi-methyl-aniline (Van Romburgh, R T C 2,106)

Reactions —1 MeCl forms only NMe, Cl and NMe, HHCl (Vincent a Chappuis, C R 102, 436) —2 SO, Cl, forms oily NMe, SO, Cl (183°—187°) and SO, (NMe,), (Behrend, B 14, 181°) — 3 Cyanamide heated with NHMe, at 110° forms di-methyl guandine (Tatarinoff, C R 89, 608) 4 p-Diazotoluene chloride forms NMe, N,O,H,

[46°] (Goldschmidt a Badl, B 22, 935) Salts —B'HCl V sol chloroform (differ ence from NH,Cl and NMeH,Cl (Behrend, B 15, 1611, A 222, 119)—B'HAuCl, needles — B'₂H₂PtCl₆ Trimetri Monoclinic Trimetric needles B',H,IrCl, Trimetric octahedra, =1 969 1 1 954 (Vincent, Bl [2] 43, 154) — B' Rh₂Cl₁₂ 3aq Large dark garnet red prisms $B'_{\mathfrak{a}}Rh_{2}Cl_{12}\,3aq$ [2] 44, 513, C R 101, $\hat{3}22$) – (Vincent, Bl B',H,HgCl, Monoclinic crystals (Topsoe, B'HHg,Cl, Monocimic crystals -Monoclinic crystals (T) — B'_H_Hg_Cl₁₂ Truclinic crystais — B'_H_SnCl₄ Trimetric tables (Hjortdahl, J. 1882, 474 — B',H,CuCl, — B',2H,CuCl, Crystals

—B'HCuCl, Monodinio crystals (T) — B'HBr

—B',2H,PtBr, Trimetric needles — B',4H,1,6BiL, -B',H,I,2BiI, (Kraut, A 210, 314) -B'HNO. [74°] Long hygroscopic needles of prisms V sol alcohol (Franchimont, R T C 2, 338, 3, 229) Decomposed by heat, yielding nitrogen, CO₃, and dimethylamine (Romburgh, R T C 5, 246) —B'HVO, (Balley, C J 45, 693) — B'₄(H₂O)₂(V₂O₃), 4aq — Benzene sulphonate [110°] (Norton, Am 10, 129) —p-Toluene sulphonate [78°] (N)

Acetylder vature NMe, Ac (186°) S G 20 941 From dimethylamine and AcCl dissolved in ether (Franchimont, R T C 2, 121, 342) Colourless liqud Fuming HNO, forms in the

cold NMe₂.NO₃ [57°]

Trs-chloro-acetyl derivative CCl₂ CO NMe₃. [104] (C) SG ¹² 1 441 (F a K) From CCl₂ CO CCl₃ and NMe₃ (Cloez, A Ch [6] 9, 145)

Heptoyl derivative C,H₁₃ CO NMe₂ (243°) S G ¹² 894 Solidifies below -10° (Franchimont a Klobbie, R T C 6, 249) With HNO₂ it gives di-methyl-nitro-amine

Valery l derivative CMe, CONMe. (185°) SG H 912 Liquid, v sol water Not solidified at -17° HNO, (SG 152) forms NMe, NO.

Bensoyl derivative C.H. CO NMe.: [42°] (256° uncor) Crystals, v sol water Split up by aqueous HCl at 200° into HOBz and

HNMe, (Hallmann, B 9, 846) Conc HNOs gives C.H.(NO.) CO NMes (Romburgh, R T C 4, 385) With COCl., it forms deliquescent crystals of C.H., CCl., NMes [386°] decomposed by water into HCl and C.H., CO NMes

D1-methyl-iodo-amine NMe₄I From dimethylamine, iodine, and NaOH Pale yellow pp, which rapidly decomposes (Baschig, A 230, 223)

Dimethylnitrosemine NMe, NO (148° at 725 mm) Formed by treating an aqueous solution of dimethylamine hydrochloride with potassium nitrite (E. Fischer, B. 8, 1587, Renouf, B. 13, 2169) Yellow oil Volatile with steam Reduced by zinc dust and HOAc to dimethyl hydrazine "Decomposed by boiling HCl into NMe, H and nitrous acid —B'HCl white needles, decomposed by water or alcohol

Di-methyl nitro amine NMe₂NO₂ [57°] From NMe₂Ac and HNO₃ (Franchimont) Large crystals

Di methyl amme tri-bromide Me₂NBr₃ 2aq or Me₂ N $\underset{\leftarrow}{\otimes} R_3$ Formed, as a yellow pp, on adding an excess of bromine water to a cold solution of dimethylamine—2Me NH + 4Bi + 2H₂O = C₂H₁₀NBr₃O₂ + Me₂NH₂Br yellow powder Sol alcohol and ether, v sl sol water It is very unstable on keeping over night in a closed vessel it liquefies to a brown fluid containing free bromine, but under water it can be kept for several days Alkalis and acids decompose it at once, thus HCl gives dimethylamine hydrochlor ide according to the equation C₂H₁₀Br₃NO₂ + 2HCl = Me₂NH,HCl + 3Br + Cl + 2H₂O (Raschig, B 18, 2249)

Trimethylamine C_sH_sN is NMe, Mol w 59 (35°) SG $\frac{-53}{662}$ (Hofmann, B 22, 703) H F p 15.870 (Thomsen, Th), 14900 (Muller, Bl. [2] 44, 609) H F v 13550 H C 577,600 (M) Heat of neutralisation (by HCl) 17,900 (Muller, A Ch [6] 15, 531)

Occurrence - In herring brine (Hofmann, C J 5, 288, cf Wertheim, J 1851, 480) In the flowers of Cratagus oxyacantha (Wicke, A 91, 121), C monogyna, Pyrus aucuparia, and P communis (Wittstein, J 1854, 479) stinking goosefoot (Chenopodium vulvaria) (Dessaignes, J 1851, 481), in Arrica montana (Hesse, J 1864, 458), and in the seeds of the beech (Brandl a Rakowiecki, J 1864, 607) It also occurs in Mercuryalis annua (E Schmidt, B 10, 2226) In human urine (Dessaignes, A 100, 218), and in calves' blood which has stood 12 hours (Dessaignes, *J. Ph.* [3] 32, 43) In ergot of rye (Walz, *J.* 1852, 552, Rithausen, *Rép.* chim pur 1863, 420, cf Brieger, H 11, 184) In small quantity in guano (Hesse, J. 1857, 402) In bone oil (Anderson, A. 80, 51) According to Ludwig (Z. 4, 96) it occurs in small quantity in several Austrian and Hungarian wines In the product of the destructive distillation of putrid brain (Selmi, G 6, 468) and of beet-root molasses (Vincent, C R 84, 1139, 85, 667, J Ph [4] 30, 132, Roscoe, C N. 39, 107). In the putrefaction of yeast (A Müller, J 1857, 402) and of wheat dough (Sullivan, J 1858, 231). In most of the cases here mentioned the trimethylamine is probably obtained from betaine, neurine, or lecithin, either by putrefactive desomposition or in the chemical treatment

Formation—1 Together with NMeH₂ and NMe₂H by the action of ammonia on MeI, and separated by treatment with oxalic ether, with which it does not react (Hofmann, C J 4, 304) 2 By the distillation of NMe₄OH (Hofmann, A 93, 325)—3 By heating narcotine with KOH at 280° (Wertheim, A 73, 208)—4 By heating extract of calamus root with alkali (Thoms, B 21, 1912)—5 By passing coal gas through heated zinc dust (Williams, C N 51, 15)

Preparation -1 The residues in the preparation of sugar from beet root are, after fer-mentation, subjected to dry distillation The mentation, subjected to dry distillation aqueous portion of the distillate is neutralised by H₂SO₄, ammonium sulphate separated by crystallisation, and, after evaporation, the trimethylamine expelled by an alkali Commercial trimethylamine still contains methylamine, ethylamine, dimethylamine, propylamine, and isobutylamine The proportion in which these bases are present varies greatly in different samples. To the aqueous solution of the bases oxalic ether is added, the primary bases being ppd as di alkyl oxamides The mother liquor is distilled with addition of KOH and the dry bases dissolved in absolute alcohol Oxalic ether is then added to the alcoholic solution, when the diamines are converted into di alkyl oxamic ethers, and the trimethylamine can be obtained by distillation (Vincent, C R 89, 238, 788, Duvillier a Buisine, C R 89, 48, 709, 92, 250, A Ch [5] 23, 298, cf Eisenberg, B 13, 1669) 2 Perfectly pure trimethylamine is obtained by distilling NMe OH and rectifying over sodium (Hofmann, B 22, 699)

Properties —Gas with ammoniacal and fishy odour Remains liquid at -75° V e sol water When an aqueous solution is strongly cooled a hydrate NMe, 7aq [43°] separates

Reactions—1 KMnO, oxidises it to CO, and oxalic acid (Wallach a Claisen, B 8, 1237)—2 At a red heat it is converted into HCy and MH,Cy (Willim, Bl [2] 41, 449) Passed with hydrogen through a red-hot tube it yields NH, cyanogen, hydrocarbons, and CH,(NMe,), (Bo meny, B 11, 835)—3 CS, forms NMe,CS, crystallising in white needles [125°] This body is m sol chloroform and dilute alcohol, nearly insol absolute alcohol, CS, and benzene It splits up into its components, even at ordinary temperatures, but with dilute HCl it forms NMe,CS,HCl and (NMe,CS,),H,Cl, Conc HClAq splits it up into its components Phosphoric acid forms (NMe,CS,),H,PO, (Bleunard, C R 87, 1040)—4 Glycol chlorhydrin forms neurine chloride NMe, ClCH, CH,OH—5 Chlorocacetic acid forms betalne CH, NMe, OS O—

6 Dichlorhydran of glycerin forms 'sepine' chloride C₃H₃Cl(OH) NMe₃Cl and 'aposepine' chloride C₃H₃(OH)(NMe₃Cl)₂ (Niemikovitch, M 7, 249) — 7. Hexa chloro-acetons forms CCl₃ CO NMe₂ [1047] (Cloëz, A Ch [6] 9, 145) 8 When heated with annine hydrochloride it yields a distillate of methyl annine

Salts—B'HCl decomposes at 285°, giving off NMe, and MeCl, and leaving mono- and dimethylamine hydrochlorides. At 305° ammonia

and methyl chloride are given off from the residue, and at 325° the whole has sublimed, the sublimate consisting of NH₄Cl and methylamine hydrochloride This decomposition may be utilised for the manufacture of MeCl (Vincent, C R 84, 1139, 85, 666) —B'HBr decomposed between 230° and 300° into NMe, ammonia, and MeBr -B'HI white scales, decomposed between 210° and 280° into NMe,, ammonia, MeI, and a residue of NMe,I—B',H,PtCl, orange regular crystals (Ludecke, J 1880, 512, Topsoe, J 1883, 618) S (alcohol) 0362 More soluble tuan the di- and still more so than the monomethylamine platinochloride (Eisenberg, A 205, 139) -B'2H_IrCl₄ reddish brown octahedra (Vincent, Bl [2] 43, 155) -B'HAuCl₄ yellow monoclinic crystals V sl sol water, sol alcohol [220°] (Hesse, J pr 71, 480, Zay, G 13, 420)
—B'₆H₆Rh₂Cl₁₂ 9aq (Vincent, C R 101, 322)— B'HCdCl, trimetric crystals (Hjortdahl, J 1882, 475)—B'₂H₂HgCl, monoclinic crystals (T)— B HHgCl, monoclinic crystals (T) -B'HHg2Cl, BHHgCl, monoclinic crystals (T) —B'HHg,Cl, the triclinic crystals (T) —B'HHg,Cl, thombothers (T) - B'HCuCl, 2aq monoclinic crystals —B'HCdBr, six sided hexagonal prisms — B'HPtBr,—B',H,I,2BiI, six sided crimson plates (Kraut, A 210, 316) —B'HNO, [153°] Long needles or prisms, v sol hot alcohol (Franchimont, R T C 2, 338) —B',H,SO,Al,(SO,), 24aq [100°] Large crystals (Reckenschufs, A 83,343)—B',(HO),(V,O),), 7aq (Bailey, C J 45, 692)—B'H,C,O, plates (Loschmidt, J 1865, 375)—Benzene sulphonate [89°] (Westenhoff, Am 10.129) phonate [89°] (Westenhoff, Am 10, 129)

Tetra methyl ammonium hydroxide NMe,OH Heat of neutralisation (by HCl) 27,900 (Muller, A Ch [6] 15, 531) Obtained by digesting NMe,I with moist Ag.O (Hofmann, Tr 1850, 93, C J 4, 321) White crystalline deliquescent mass, v e sol water Absorbs CO₂ with avidity Its solution is strongly alkaline and caustic Decomposed by heat into NMe, and MeOH (Hofmann, B 14, 494) Neutralises acids, forming the following salts

Icdatde NMe,I S G H 1827, 19.5 1831 (Clarke, Am S [3] 16, 401) The chief product of the action of MeI on ammonia and on mono, di, and tri methylamine Best obtained by heating a solution of NH, in methyl alcohol with MeI at 100°-120° (Lawson a Collie, C J 53, 624) Dimetric prisms (from water) S sol water, almost insol alcohol, insol ether Decomposes at a dull red heat into NMe, and MeI Unites with iodoform forming red crystals of NMe,I2CHI, When heated with liquefied NH,, in which potassium has been dissolved, the products are KI, NMe, and ethane (Thompson a Cundall, C J 53, 761) Unites with halogens, forming NMe,I, (Welzien, A 91, 41, 99, 1), NMe,I, [130°], NMe,I, [110°] (Geuther, A 240, 68), NMe,I,, NMe,ICl., (NMe,I),Cl., (W), NMe,IBr, [190°] (Dobbin a. Masson, C J 49, 851), and NMe,ICl., [100°] (Dobbin a. Masson, C J 49, 851), and NMe,ICl., [110°] (Me,I), a dark-coloured explosive body (Stahlschmidt, P 119, 421) — NMe,IGI, small light-yellow prisms, m sol alcohol—(NMe,I),8HgI, lemonyellowscales (Risse, A 107, 223)—(NMe,I),2BII,32mI,32morphous scarlet pp (Kraut, A 210, 316)—NMe,IHgCy, white crystals On heating for a

long time at 200° it is converted into the isomeric

NMe CyHgICy (Claus a Merck, B 16, 2738) Bromide NMe, Br S 55 26 at 15° tained by neutralising the hydroxide by HBr Very deliquescent needles Dissociates at 360° into NMe, and MeBr (Lawson a Collie, C J 53, Forms crystalline compounds with the halogens (Dobbin a Masson, C J 49, 848) — (NMe,Br),PtBr, regular octahedra (Topsoe)
Chloride NMe,Cl H.F 27,500 (Müller, Bl

[2] 44, 192) Deliquescent crystals Decomposed above 360° into NMe, and, doubtless, MeCl (L a C) — (NMe,Cl),HgCl, trimetric crystals (T) — NMe,Cl5HgCl, rhombohedra — (NMe,Cl),CuCl, trimetriccrystals — NMe,AuCl, trimetric dimetric crystals

Fluoride NMe,F From the hydroxide and

HF Radiating crystals Decomposes at 180° into NMe, and MeF (L a C)

Nutrate NMe, NO, S (94 pc alcohol) 3 at 11° Obtained, together with NMeH, NO, NMe₂H₂NO₃, and NMe₃HNO₃ by heating methyl nitrate with NH₂ dissolved in MeOH (Duvillier a Busine, C R 90, 872) The di and tri methylamine are formed in very small quantity (Duvillier a Malbot, C R 100, 177) Formed also by treating NMe,I with AgNO, (Lawson a Collie, C J 53, 628) Needles or plates, v sol water, sl sol cold alcohol Not attacked by boiling KOHAq Above 300° it yields NMe, formic acid, MeNO, and NO (L a C)

Nitrite NMe, NO. From NMe, I and AgNO. Deliquescent crystals Decomposed above 300° into NMe, MeNO, MeO, NO, and oxygen (L a.

Sulphate (NMe,),80, [280°] Deliques at crystals Decomposed above 280° into cent crystals MMe, and NMe, SO, Me, which then undergoes

further decomposition (L a C)

Chromates (NMe.) CrO, yellow trimetric crystals, v e sol water (Hjortdahl, J 1882, 475) -(NMe₄)₂Cr₂O₇ orange trimetric tables, v sol water

Sulphite NMe, SO, H xaq [180°] Decomposes above 300°, yielding NMe, SO, MeOH, and other products (L a C)

Sulphydrate NMe SH Very deliquescent Decomposes above 200° into NMe, and MeSH

Phosphate From NMe,I and Ag,PO,
Forms a strongly alkaline solution Decomposed at a high temperature into NMe, methyl alco-

hol, and HPO, (L a C

Vanadate NMe, VO, (Bailey, C J 45, 693) Carbonates NMe, CO, H HF 20,870 HF 20,870 (Muller) Obtained by saturating a solution of the base with CO₂ (L a C) Deliquescent crys tals, decomposing above 180° into NMe₂, methyl alcohol, and CO_2 — $(NMe_s)_2CO_3$ HF 19,100 Obtained by acting on NMe₄I (2 mols) with Ag_2CO_3 $\frac{1}{10}Ag_3O$ (Muller, Bl [2] 44,191)

 $(NMe_4)_2C_2O_4$ Oxalate Formed NMe,OH and oxalic acid, or from NMe,I and silver oxalate Deliquescent crystals, decomposed above 860° into NMe, and methyl oxalate, the latter being further resolved into Me₂O, CO,

and CO,

Cyanide NMe, Cy Prisms Sublimes at 226° V sol water, m sol alcohol, insol ether and chloroform (Claus a Merck, B 16, 2738)
—NMe,CyHgCy, [275° uncor] Yellow crys-Yellow crystals — NMe, CyAgCy. [212° uncor] From AgCy

and NMe,I or NMe,Cy (Thompson, B 16, 2338) Long colouriess prisms or slender needles, v e sol water and alcohol, insol. ether On dry distillation it yields NMe, acetonitrile, and methyl carbamine

Ferrocyanides (NMe,), FeCy, 13aq mino granular mass (Barth, B 8, 1484) — (NMe.)₂H.FeCy, 2aq (E Fischer, A 190, 184)

Ferricyanide (NMe,) FeCy, 3aq From NMe, I and silver ferricyanide (Bernheimer, B 12. 408) Unstable hygroscopic prisms, sol water, insol alcohol

Cobalticyanide (NMe.), CoCy, 13aq Yel

low tables (C a M)

Acetate NMe,OAc [c 70°] From NMe OH and HOAc Deliquescent needles, de composed at 200° into NMe, and MeOAc (L a.

Benzoate NMe₄OBz [220°-230°] Long deliquescent needles Decomposed above 230° mto NMe, and MeOBz (L a C)

Cyanurate NMe,OC,N,(OH), aq (Claus,

 $J pr^{-}[2] 38, 225)$

Picrate [313°] (Lossen, A 181, 374)
Trimethylamine iodo-methylo iodide

NMe, I CH, I From NMe, and methylene iodide (Hofmann) Needles Not attacked by NH, Moist silver oxide gives NMe, (OH) CH2I and NMe(OH) CH, OH It yields the platinum salt

PtCl₄(NMe₄Cl CH₄I),
Trimethylamine ethylo-iodide C₅H₁₄NI 26 NMesEtI From NMes and EtI (Muller, A 108, 1) Gives the following derivatives (Topsoe, J 1883, 620) — (NMe,EtCl),2HgCl, trimetric crystals — NMe,EtClHgCl, monoclinic crystals — NMe,EtCl(HgCl), trimetric crystals — (NMe,EtCl),CuCl, trimetric crystals —Aurochloride NMe,EtAuCl, dimetric crystals — (NMe,EtCl),PtCl, regular crystals—Picrate [300°] (Lossen, A 181, 374) The ethylohydroxide is decomposed on distillation into NMe₃, ethylene, and water NMe₃LtCl on dis tillation yields MeCl, NMe,Et, and NMe,

Trimethylamine ethylo tri-iodide NMe,EtI, Pagular crystals (Ludecke, A 240, 85)
Tri-methylamine ethylo penta iodide NMe₃EtI, [26°], dark green tables (Geuther, A 240, 66)

Trimethylamine ethylo ennea-iodide NMe₃EtI, [38°], black green crystals

Trimethylamine bromo-ethylo bromide C₂H₄Br NMe₃Br From NMe₃ and ethylene bromide at 45° (Hofmann, C R 47, 558) Needles, v e sol hot alcohol Ammonia as well as moist Ag₂O converts it into C₂H₃ NMe₃OH -(C.H.Br NMe,Cl),PtCl, Octahedra C.H.Br NMe,I (Baeyer, A 140, 312) Octahedral crystals -

Trimethylamine 10do ethylo 10dide C.H.I NMe.I From neurine, HI, and phos phorus (Baeyer, A 140, 309, 142, 324) Crys talline, sl sol cold water Moist Ag,O yields C₂H₃.NMe₃OH — (C₂H₄I NMe₃Ol)₂PtCl₄ hedra

Trimethylamine allylo bromide C.H. NBr 2 & NMe₂C₂H₂Br Forms a dibromide NMe₃C₃H₂Br₁ [175°] of which the gold salt melts at 148° (Partheil, B 22, 3317)

Trimethylamine bromo-allylo-bromide NMe,Br CH2.CH CHBr [165°] Formed from NMe,C,H,Br, and alcoholic KOH Colourless prisms v sol water and alcohol, insol ether, gives a perbromide NMe,Br CH,CHBr CHBr, erystallising in scales [156°] --Platinochloride (C,H,Br NMe,Cl),PtCl, [220°] -- Aurochloride C,H,Br NMe,AuCl, [181°]
Trimethylamine propylo-iodide NMe,PrI

[190°] (Langeli, G 16, 385)

Trimethylamine iodo-propylo-iodide

NMe₃I C₂H₃I [151°] From the allylo iodide and HI at 100° (Partheil, B 22, 3320) Colourless needles, sol water and alcohol, insol ether Alcoholic KOH regenerates the allylo-com-[237°] —Auropound — (C,H,I NMe,Cl),PtCl, chloride (C,H,I NMe,Cl)AuCl, [135°]

Trimethylamine trimethenyl bromide

 $\mathbf{c}\mathbf{H}$ From the bromo allylo-NMe₃Br CH ĊΗ bromide and alcoholic KOH.-Aurochloride

(NMe, Cl C, H,)AuCl, $\mathcal{C}\mathbf{HBr}$

Dibromide NMe,Br CH [187°] ĊНВr

From the preceding and Br Colourless, somewhat hygroscopic crystals Forms a platinochloride [232°] and an aurochloride [193°]

both crystallising in tables

Trimethylamine bromo-pentenyl bromide C.H.BrNMe.Br Formed from trimethylamine and di bromo amylene (valerylene bromide) (Ladenburg, B 14, 231, 1342) With HI it forms C.H., BrNMe, I Silver chloride forms C₅H₈BrNMe₃Cl, whence (C₅H₈BrNMe₃Cl)₂PtCl₄ and C.H.BrNMe.ClAuCl., both crystalline

Trimethylamine isoamylo triiodide NMe₃C,H₁₁I₂ [80°] From NMe₄ and the product being treated with iodine [80°] From NMe, and C,H,I, Darkbrown prisms, nearly insol water, v sol alcohol

TRIMETHYLAMMELIDE v vol 11 p 325 DI-METHYL-AMMELINE v vol 11 p 321 METHYL-AMYL-ACETAL & ALDEHYDE

METHYL-ISOAMYL-ANILINE C₁,H₁,N te C₅H₅NMe C₅H₁₁ (257°) S G ²² 906 Obtained together with C,H₄ and water by distilling C₆H₃NMeEtC₅H₁₁OH (Hofmann, A 79, 15) Formed also by heating dimethylaniline with isoamyl bromide (Claus a Rautenberg, B 14,

622) —B'₂H₂PtCl₆ crystalline pp —(B'HI)₂Bil₃ METHYL AMYL ARSINE v Organic com-

pounds of Arsenic

METHYL AMYL BENZENE AMYL

Di methyl isoamyl benzene v AMYL XYLENE METHYL - ISOAMYL - BENZENE SUL-PHONIC ACID CH, C,H,(C,H,) SO,H From p isoamyl toluene by sulphonation (Fittig a Bigot, A 141, 166) -KA' The Ba salt is a deliquescent gummy mass

Di methyl isoamyl benzene sulphonic acid (OH₃), C₆H₂(C₅H₁₁)SO₂H Formed by sulpho nating isoamyl-xylene (F a B) The K and The K and

Ba salts were not obtained in crystals

METHYL AMYL CARBINOL HEPTYL ALCOHOL

DI METHYL AMYLENE DIKETONE

C₂H₁,O₂ *e CEt₂(CO CH₂)₂. Di ethyl-acetyl acetone (c 203°) From (CH₂ CO)₂CEtNa and EtI at 180° (Combes, A Ch. [6] 12, 250) Liquid Split up by KOH into CH₂ CO₂K and OH, CO OHEt,

Di methyl amylene diketone C.H.O. ie (CH,CO CH,CH,),CH, Di acetyl-pentane

[49°] (212°-215° at 300 mm) From the carboxylic ether and a dilute solution of KOH in MeOH (Kipping a Perkin, C J 55, 337) ▼ sol cold ether, alcohol, acetone, chloroform, and light petroleum Cold cone HNO, dissolves it without decomposition Conc H2SO, forms a colourless oil C.H.O

Dioxim (CH, C(NOH) CH, CH,), CH, [85°], Colourless moss like crystals, v sol cold water DI METHYL AMYLENE DIKETONE CAR-

BOXYLIC ACID

CO₂H CHAo CH₂.CH₂ CH₂ CH₄ CO CH₃ From Liquid, its ether and KOH dissolved in MeOH miscible with water Decomposed by heat into CO₂ and the diketone

Ethyl ether EtA' (240° at 200 mm) Prepared from sodium aceto acetic ether and CH, CO CH, CH, CH, CH, Br (Kipping a Perkin, C J 55, 333) Thick oil Alcoholic NH₃ con verts it into Ac CH2 CH, CH2 CH2 CMe NH [c 235°], which forms monoclinic crystals, $a b c = 7487 1 3997, \beta = 79^{\circ}11'$ This 'dehydro amide ' yields an acetyl derivative C10H14AcNO. an oil, converted by boiling water into the amide CH, CO CH, CH, CH, CH, CH, CH(COMe) CONH, which melts between 200° and 228°

METHYL AMYL ETHER v METHYL AMYL OXIDE

METHYL AMYL KETONE CHIO 16 CH, CO CH. CH. CH CH. CH, (151°) 2 837 Formed by oxidising sec heptvl alcohol obtained from n heptane (Schorlemmer, A 161, 279, 217, 149) Fragrant liquid Unites with NaHSO, Yields on oxidation acetic and n valeric acids Formed also by dissolving heptinene C₅H₁₁ C CH in conc H₂SO₄, and distilling the product with water (Behal, 4 Ch [6] 15, 270)

Methyl isoamyl ketone C H₁₁O ie CH₁ CO CH₂ CH₂ CH(CH₂)₂ (144°) S G ² 828, Lt 818 (Rohn, A 190, 308), ² 821 (Wagner, J R 16,705)

Formation —1 By heating a mixture of calcium hexoate with calcium acetate (Schmidt, B 5, 604) -2 By the action of zinc isoamyl on acetyl chloride (Popoff, A 145, 283) -3 By oxidising the corresponding heptyl alcohol (Grimshaw A 166, 169) -4 By boiling isobutyl aceto acetic acid with aqueous KOH the yield

being 70 pc (Puidie, C J 39, 467)

Properties —Oil Reduced by sodium to sec heptyl alcohol and di isopropyl pinacone CrO, oxidises it to acetic, isovaleric, and isohexoic acids. It combines with NaHSO.

Methyl amyl ketone Me CO CHMePr (142°-From methyl propyl aceto acetic ether (E J Jones, A 226, 293) Oil, smelling of pepper-

Methyl amyl ketone CH, CO CHMePr (135°) S G 22 815 One of the products of the saponification of methyl isopropyl aceto acetic ether (Van Romburgh, R T C 5, 235) Does not combine with NaHSO, Does not give a solid phenyl hydrazide

Methyl amyl ketone CH, CO CH, CMe, (125°-130°) Obtained by oxidising the alcohol CMe, CH2.CMe2 OH (Butlerow, A 189, 78) Oxi dised by CrO, to acetic acid and CMe, CO,H Does not combine with NaHSO

Methyl amyl ketone CH₃ CO CHEt₂. (138°), S G 22 817 Obtained by boiling di ethyl acetoacetic ether with baryta water (Frankland a Duppa, A 138, 212) Forms an oily compound

with NaHSO.

Methyl amyl ketone CH, CO CMe, Et Methyl-(132°) SG 2 842, 21 825 amyl-pinacolin Obtained by the action of ZnMe, on CMe, Et COCl (Wyschnegradsky, A 178, 103) CrO, oxidises it to HOAc and CMe, Et CO, H

Methyl amyl ketone CH_a CO C_aH₁₁ From sec-heptyl alcohol derived from petroleum heptane (90°) Gives acetic acid on

oxidation (Schorlemmer, A 166, 172)

Methyl isoamyl diketone CH, CO CO C,H, Methyl isoamyl-glyoxal (163°) S G 19 8814
From methyl nitrosohexyl ketone (Otto a Pechmann, B 22, 2123) Oil, solidified by cold

White Phenyl-hydraside

needles (from benzene ligroïn)

Di-phenyl-di hydrazide. Needles (from dilute alcohol) [114°]

Di-oxim [173°] Needles

Oxem-phenyl-hydraside [132°] White

needles (from benzene ligroin)

METHYL AMYL KETONE CARBOXYLIC ACID CH, CO CH, CH, CH, CH, CH, CO, H [30°] A product of the action of a boiling solution of KOH in MeOH upon dimethyl-amylene diketone carboxylic ether (Kipping a Perkin, jun, C J 55, 338) Also from sodium malonic ether and CH, CO CH, CH, CH, CH, CH, Br, the resulting dicarboxylic acid being distilled talline plates, v sol water -AgA' colourless

METHYL ISO AMYL OXIDE C₆H₁₄O 1 e (A O C.H., Mol w 102 (92°) V D 3 74 CH₃ O C₄H₁₁ Mol w 102 (92°) V D 3 74 S V 148 I (Schiff) From McONa and isoamyl

iodide (Williamson, C J 4, 233)

METHYL-AMYL-PIPERIDINE C11H23N 2 e $C_sH_9N(C_sH_{11})(CH_8)$ (190°-193°) Prepared by dry distillation of the alkaline hydrate obtained by the action of moist Ag₂O on amyl piperidine methylo iodide (Schotten, B 15, 422) Colourless fluid Sl sol water With Mel it forms a crystalline methylo iodide -B'HCl hygroscopic salt —(B'HCl)2PtCl4 sparingly soluble pp, melts at [140°]

METHYL AMYL SULPHIDE CH, S C, H, (137°)VD 586 From NaSC, H, and MeI

(Obermeyer, B 20, 2924)

METHYL AMYL DI-THIO-CARBONATE $^{\times}$ CO(8Me)(SC₃H₁₁) (c 140°) From Cl CO SC₃H₁₁ and NaSMe (Schöne, J pr [2] 32, 244) Liquid, smelling like CS₂ With ammonia it gives HSC,H₁₁, ures, and HSMe Alcoholic potash forms K₂CO₃, methyl mercaptan, and HSC,H₁₁ METHYL-ANHYDRO-ACETONE-BENZIL v.

METHYL-ANILINE C.H.NHMe Mol w (193° uncor) (Friswell a Green, B 19, S G 15 976 H F -5500 H C v 2035 973,000 (Petit, C R 107, 266) Heat of neutralisation (by HCl) 6,910 (Vignon, C R 106, 1722)

Formation -1 Together with dimethylaniline from aniline and MeI or MeBr (Hofmann, A 74, 150, B 10, 591, of Kern, B 10, 195)—2 Together with dimethylaniline by heating methyl alcohol with aniline and HOl at 200° ander pressure (Girard, Bl [2] 24, 120, cf Poirmer a. Chappat, J 1866, 903) —3 By heating aniline hydrobromide (or hydroiodide) with 10 p.c. more than the calculated quantity of methyl

alcohol to 150° for 8 hours, the yield is 34 p c of the theoretical (Reinhardt a Staedel, B 16, 29, of Kramer a Grodzky, B 13, 1006) —4 By heating acetanilide with alcoholic sodium ethyl ate at 170°-200° under pressure (Seifert, B 18, 1355) -5 By adding sodium to a solution of acetanilide in xylene, treating the resulting sodium-acetanilide with MeI and boiling the pro duct (C_sH₅NMeAc) with alcoholic potash (Hepp, B 10,327) -6 From its formyl derivative (Pictet a Crépieux, B 21, 1108) -7 By boiling diazo benzene methyl anilide (100 g) with conc HCl (200 c c), making alkaline with NaOH, and dis tilling with steam, yield 40 g (Friswell a Green, B 19, 2035)

Purification -By the action of MeOH and HCl on aniline a mixture of bases is obtained On adding dilute H₂SO₄ aniline sulphate sepa rates, and the bases liberated from the filtrate may then be heated with AcCl On pouring the product into water the acetyl derivative of methyl aniline separates in long needles, while dimethyl aniline hydrochloride remains in solution The acetyl derivative may be quickly saponified by boiling with conc HClAq (Hofmann, B 7, 523) The mixture of bases may also be treated with nitrous acid, whereby a diazo benzene salt, phenyl - methyl - nitrosamine, and nitroso di methylaniline are formed The nitrosamine, being insoluble in water and acids, separates as a yellow oil, and may be reconverted by tin and HCl into methyl aniline (Noelting a Boasson, Bl [2] 28, 2)

Properties -Oil Its aqueous solution is not coloured by bleaching powder With NaOBr it gives a yellow pp (Denigès, C R 107, 662) With CuSO, it forms a compound B'(CuSO,),4CuO

(Lachovitch, M 9, 514)

Estimation —1 It is treated with a mixture of Ac₂O (1 vol) and di methyl aniline (10 vols), water is added after the reaction, and the solu tion titrated with phenol phthalein The di methyl aniline does not interfere with the reac tion, and the mixture of it with the acetic anhy dride keeps well (Giraud, Bl [3] 2, 142) -2 In a mixture of aniline, methylaniline, and dimethyl aniline the aniline is first determined by diazo tisation and ppn by (B) naphthol disulphonic acid (R) and NaClAnother portion of the mixed bases (2 g) is mixed with Ac₂O (4 g), and, after 30 minutes water (50 c c) is added liquid is boiled to decompose the excess of Ac2O, and the acid solution titrated with Na₂CO₃ using phenol phthalein as indicator. The amount of Ac₂O found plus that required by the aniline pre viously determined is then subtracted from the amount taken, and gives a measure of the methylaniline present (Reverdin a De la Harpe, B 22, 1004) —3 In a mixture of mono- and di methyl aniline the amount of the former present may be known by observing the rise of temperature on mixing with an equal volume of Ac. C

Reactions —1 HNO, gives off red fumes con taining CO2, and forms tetra-nitro-methyl aniline (Van Romburgh, R T C 2, 31) -2 NaNO₂ added to a solution of its hydrochloride forms phenyl-methyl-nitrosamine C_eH_o NMe NO, a yellow oil solidifying when cooled as needles [12°-15°] It gives no reaction with gallic acid (Reverdin a De la Harpe, B 22, 1006) -8 Boiling sulphur forms methenyl amido-phenyl mercaptan and crystalline C_sH₇NS₂ [89°] (360°) (Möhlau a Krohn, B 21, 59) -4 A solution of methylaniline sulphate saturated with SO, forms with an aqueous solution of alloxan small yellowish prisms of CO NH CO C(OH) SO, NH, PhMe 2sq (Pellizzari, A 248, 148) —5 An aqueous solution of alloxan forms (C₄H₂N₂O₄)(NHPhMe), a compound crystallising in white scales, with a hydro-chloride crystallising in prisms — 6 Diazobenzene chloride and aqueous NaOAc form PhNMe N NPh, a yellowish oil, decomposed by dilute H2SO, into diazobenzene sulphate (or phenol) and methylaniline, and by SnCl, and HCl into phenyl hydrazine and methyl aniline (Nölting a Binder, B 20, 3017) -7 p-Nitro-diazobenzene chlorade and NaOAc form CaH, (NO2) N N CaH, NHMe crystallising in red needles [134°], v sol hot alcohol (N a B) -8 Bromo-acetophenone forms C₆H₅ CO CH₂ NPhMe in the cold, and on boiling it gives phenyl indole and phenyl methyl-indole (Cullmann, B 21, 2595)

Salts -B'2H2PtCl Yellow scales Decom posed by boiling water (De Coninck, Bl [2] 45, 131) —B'HCdBr₃ Trimetric crystals (Hjortdahl, J 1882, 522) —B'₂H₂SnBr₆ Monoclinic crystals —B'HSO₄Me Needles (Claesson a Lundvall,

B 13, 1703)

Formyl derivative CaHaNMeCHO [12 5°] (N a L) (250°) (N a L), (256°) (Pictet a Crépieux, B 21, 1108) S G 3 1097 From (NaL) From sodium formanilide and MeI (Norton a Livermore, B 20, 2273) Formed also from methylaniline and the hydrochloride of formimido ether (Pinner, B 16, 1652) Oil, could not be solidified by Pictet When boiled with 121 pc nitrio acid it yields dinitromethylaniline

Acetyl derivative C.H.NMeAc Exalgin.' [1015°] (Kamensky, A 214, 236) (256°) (P a C) Formed from sodium acetanihde and MeI (Hepp, B 10, 328, Hofmann, B 10, 599) Formed also by the action of acetyl bromide on dimethylaniline (Staedel, B 19, 1947) White needles and tablets, sl sol cold water, v sol dilute alcohol As a medicine it has an energetic action on the cerebro spinal system (Dujardin Beaumetz, C R 108, 571, cf Giraud, C R 108, 749) It is a good antiseptic Boiling nitric acid forms (4, 2, 1)-di nitro methyl aniline

Thio acetyl derivative CH, CS NPhMe [59°] (290°) From the acetyl derivative and sulphide of phosphorus (Wallach, B 13, 528) Monoclinic plates (from CHCl₃) Insol. water and alkalis, sol alcohol and ether

Propiony l derivative CH₂ CH₂ CO NPhMe [58 5°] From sodium proponantilde and MeI (Norton a Allen, B 18, CH, CH, CO NPhMe With boiling HNO₃ (100 pts of SG

1 029) it yields (4, 2, 1) di-nitro methyl aniline Oxalyl derivative (CO NPhMe), (250°) Forms oxalic acid, alcohol, and methylaniline (Norton a Livermore, B 20, 2273) Boiling nitric soid converts it into di nitro-methylaniline

Bensoul derivative C.H.NMeBz From methyl-aniline and BzCl (Hepp, B 10, Formed also by heating di methyl aniline with benzoyl chloride at 180° (Hess, B 18, 685) Large monoclinic crystals, insol water, but v

sol other solvents Gives a mono nitro-deriva tive [136°]

Nitrosamine PhMeN NO [120-150] From methylaniline hydrochloride and aqueous NaNO, (Hepp, B 10, 329, Fischer, A 190, 151, Reverdin a De la Harpe, B 22, 1006) Yellow oil, solidified by cold Reduced by tin and HCl to Gaseous HCl passed into its methylaniline solution in alcohol ether forms the isomeric [4 1]NO C₆H₄ NHMe [118°] which crystallises from water in prisms, v sol alcohol, and is converted by heating with aqueous NaOH into p nitrosophenol and methylamine (Fischer a Hepp, B 19, 2991)

Di-methyl-aniline C₆H₅NMe₂. Mol w 121 [2°-2 5°] (Friswell a Green, private communica tion) (193°) S G $\frac{20}{4}$ 9575 $\mu_{\rm p}=1$ 559 (Bruhl, A 235, 14) SH (9°-82°) 443 (Schiff, G 17, 286) Heat of neutralisation (by HCl) 6,810 (Vignon, C R 100, 1722) Formed by heating Formed by heating aniline with MeI or MeCl

Preparation -1 Aniline hydrobromide (or hydroiodide) is heated with (2 mols + 10 pc excess of) methyl alcohol to 150° for 8 hours, the yield is 95 p c of the theoretical (Reinhardt a Staedel, B 16, 29, cf Lauth, Bl 7, 448) -2 Aniline (18 pts) saturated with HCl is mixed with a further quantity (75 pts) of aniline and methyl alcohol (75 pts) The mixture is heated at 230° in closed vessels until the internal pressure falls The use of a comparatively small quantity of HCl avoids the formation of toluidine and allows of the use of iron vessels The HCl is sometimes replaced by H. SO, (Schoop, Chem. Zert 11, 253)

Purification - Dimethylaniline can be separated from methyl aniline by the methods de scribed under methyl aniline It can also be purified by freezing (Hubner, A 224, 347)

Reactions -1 When its vapour is passed through a red hot tube it forms benzonitrile (25 pc), carbazole, NH_s, benzene, and HCy (Nietzki, B 10, 474) -2 When heated in a current of HCl at 180° the products are MeCl and aniline (Lauth, B 6, 677) -3 With sodium hypobromite it gives a greenish yellow pp in the cold and a red pp on heating (Deniges, C R 107, 662)—4 Bromme (1 mol) at 115° forms methyl violet and naphthalene (Brunner a. Brandenburg, B 11, 697)—5 By nitration with a mixture of equal volumes of ordinary conc HNO, and water at 0° di nitro di-methyl aniline $C_nH_n(NO_2)$, NMe [4 2 1] is formed (yield 116 p c) If the mixture is allowed to get warm another di nitro di methyl aniline [probably 531] is formed (yield 15 pc) By further nitration of the first isomeride by boiling it with fuming nitric acid tri nitro phenyl methyl nitramide $C_8H_2(NO_2)_3NMe(NO_2)$ [6 4 2 1] is produced the same treatment the second isomeride is converted into di nitio phenyl methyl nitramide C_cH_s(NO₂)₂NMe(NO₁) [5 3 1?] (Mertens, B 19, 2123, cf Romburgh, R T C 2, 31) When nitrated in presence of a large excess of H2SO4 (20 pts) it yields as chief product the m nitroderivative whilst the p nitro derivative is formed in smaller quantity (Groll, B 19, 198, Nölting, B 19, 545) -6 Combines with aluminium chlorids with great evolution of heat forming long prisms [88°] (H Giraud, Bl [3] 1, 691).

Heated in sealed tube with 5 pts of aluminium chloride for 10 hours at 250° no change is effected. Heated in air with excess of aluminium chloride it yields a tetra methyl benzidine (CH₃)₂NC₅H₄ C₈H₄N(CH₃)₂, small needles [195°]. This base is split at 180° by action of HCl gas into methyl chloride and benzidine [118°] —7. Nitric cacide passed for 12 days into a solution of dimethylaniline (500 g.) in absolute alcohol (510 g.) forms NMe₂-C₄H₄ N N C₅H₄ NMe₂. After 3 or 4 weeks' passage of the gas there are formed a base C₁₆H₂₈N₂ [173°] and a violet colouring matter C₁₆H₂₈N₃O₃(?) (Lippmann a Lange, B 13,2136) 8 Nitrous acid forms introso di methyl aniline (g. v.) —9 By heating with sulphur there is formed a compound C₈H₁NS, which is converted

the nitrate B'HNO₃ crystallises in colourless needles and the platinochloride B'₂H.PtCl₆ in plates (Mohlau a Krohn, B 21, 65) The com pound C₈H,NS₂ is neither acid nor basic and

89° and forms prisms, insol water, and volatile On heating with sulphur it is conwith steam verted into methenyl amido phenyl mercaptan 10 Chloride of sulphur forms tetra methyl di amido di phenyl disulphide $S_2(C_0H_4NMe_2)_2$ (Hannimann, B 10, 403)—11 Heated with persulphocyanic acid it gives S(C₂H₁NMe₂), with simultaneous formation of thiocyanic acid, CS, H₂S, and NH₃ (Tursini, B 17, 586) —12 Mixed with CS, and then treated with zinc dust and HCl it gives tetra-methyl di amido di phenyl methane [90°] and thioformic paraldehyde [212°] (Wiernik, B 21, 3204) —13 Oxidising agents give rise to penta methyl tri amido tri-phenyl carbinol (methyl violet) (O a E Fischer, B 11, 2099) —14 COCl. forms CO(C, H,NMe,)₂ and, at 120°, NMe, C,H₃(ÖO C,H₄NMe)₂ —15 CCl. gives at 180°C (C,H₄NMe)₄ (Hannimann, B 10, 1689) 16 Chloroform at 230° yields CH(C,H₄NMe)₃ (Hanimann, B 10, 1235) —17 Chloral hydratein presence of ZnCl2 forms CCl3 CH(OH) C6H,NMe2 (Knöfler a Boessneck, B 20, 3195) —18 Fur furaldehyde in presence of zinc chloride yields C₄H₃O CH(C₆H₄NMe₂)₂which crystallises in pale yellow needles [83°] and is a strong base (O Fischer, A 206, 141)—19 With heptoic aldehyde and ZnCl, it also forms a condensation-product (Auger, Bl [2] 47, 42) -20 Benzoic aldehyde and ZnCl, forms C,H, CH(C,H,NMe2), (O Fischer, B 10, 1624) —21 When treated in the cold with acetyl bromide it becomes hot and yields acetyl mono methyl aniline (Staedel, B 19, 1947) -22 Heptoyl chloride in presence of ZnCl₂ forms a base [72 5°] (278° at 15 mm) (Krafit, B 19, 2987) -23 By heating with benzoyl chloride at 190°, benzoyl methyl aniline is formed with splitting off of MeCl (Hess, B 18, 685, cf Michler, B 9, 1899) -24. Benzoic acid (1 mol) and P₂O₅ at 200° forms di-methyl amido-benzophenone [88°] (O Fischer, A 206, 88) -25 Phthalic anhydride in presence of ZnCl₂ forms di-methyl-aniline phthalein —26 Benzotrichloride forms 'malachite green'

(NMe, C,H,),CCI C,H, The same body is formed (NMe₂ C₂H₃),CO C₂H₃. The same body is formed by the action of Bz₂O or BzCl in presence of P₂O₂—27 Orthoformic ether and ZnCl, form CH(O₂H₂NMe₂), —28 Vanillin and ZnCl, form C₂H₂₂N₂O₂ [136°] (Fischer a Schmidt, B 17, 1895)—29 A blue compound is obtained by the oxidation of dimethylaniline with chloranil or other chlorinated quinone It appears to have the same constitution whichever chloro quinone is used, as on reduction it always gives a leuco base of the formula C18H20N2 and melting point [173°] The latter forms glistening plates, sl sol cold alcohol, v sol hot alcohol, benzene, and ether It forms the salts B'H2Cl2 colourless crystals —B'H2Cl2PtCl4 fine needles -B"Me,Cl, crystals, sol water, sl sol alcohol, with wet Ag₂O it gives an alkaline fluid (Meister, Lucius, a Bruning, B 13, 212, 2100, Wichelhaus, B 14, 1952) -30 Acetone saturated Acetone saturated with SO₂ forms (O₃H₂O)(SO₂)(NMe Ph) crys tallising in lustrous plates, v sol water and alcohol, insol acetone (Boessneck, BAcetone and ZnCl₂ at 150° forms 21, 1906) CMe₂(C₀H₄NMe₂)₂ [83°] (Doebner, B 12, 810) — 31 Di methylaniline dissolved in a saturated solution of SO2 and mixed with an aqueous solution of alloxan forms (C4H2N2O4)(NMe.Ph)H.SO, 4aq crystallising in monoclinic plates, a b c = 1 3399 1 3394, $\beta = 93^{\circ}$ 23' (Pellizzari, A 218, 148, G 18, 329) -32 A saturated aqueous solu tion of alloxan forms a compound C, H13N3O, aq crystallising in colourless needles, sl sol water, decomposing at 250° (Pellizzari, G 17, 409) The compound forms a crystalline hydrochloride, nitrate, and oxalate, and yields a silver salt $C_{12}H_{12}AgN_3O_4$ It is decomposed by alkalis forming a compound $C_{11}H_{12}N_{12}O_{3}$, decomposing at $281^{\circ}-33$ s-Trinitrobenzene forms a com pound NMe, PhC, H, (NO2), [108°] which crystal lises in long dark violet needles, sl sol alcohol (Hepp, A 215, 358) - 34 Tri nitro toluene forms a corresponding body (H) -35 Tri nitro antline forms NMe2PhC6H3(NO2)2(NH) [141°] (Hepp)

Salts—Dimethylaniline is apparently less basic than aniline, for if a mixture of the bases is treated with an insufficient quantity of cold aqueous HCl the base left uncombined is chiefly dimethylaniline (Morley, C J 51, 580)—B'H₂SO₄ [80°] Sol water, insol ether and benzene HF 8400 The normal sulphate could not be formed At 190° the acid sulphate splits up into CO₂ and the sulphonic acid (Vignon, C R 107, 263)—B'₂H₂HgCl₄ [149°] Large tables or prisms, sol hot water and hot alcohol Prepared by adding aqueous HgCl₂ to an alcoholic solution of dimethylaniline (Klein, B 11, 1741)—B'₂Hg₂OCl₂ Formed together with the preceding Small needles or glistening leaflets, m sol hot water and hot alcohol, insol cold water, v sol benzene On heating to 100° a blue colouring matter is formed—B'₂HgCl₂ (Leeds, J 1882, 504)—B'₂H₂SnCl₄ Large monoclinic crystals (Hjortdahl, J 1882, 523)—B'₂H₂PtCl₃ Tables—B'₂H₂PtGl₄ (Reinhardt a Staedel, B 16, 29)—B'₂H₂PtBr. Brownish red monoclinic needles—Bil₄2B'HI (Kraut, A 210, 324)—(Bil₃)₃B'HI — (Bil₃)₄B'HI — (Bil₃)₅B'HI — (Bil₃)₅B'HI — (Bil₃)₅B'HI — (Bil₃)₅B'HI — B'₂H₃FeO₃ Lamins, sl. sol cold water, being less soluble than the methylaniline

and antline ferrocyanides (Fischer, A 190, 184) —

B'₂H₄FeCy₂2aq (Eisenberg, A 205, 266) Methylo-rodide C₆H₄NMe₄I Phenyl tri-methyl-ammonium rodide S (alcohol) 22 at 8° The combination of PhNMe, and MeI takes place rapidly (Lauth, Bl 7, 448) It may also be obtained by shaking a mirture of aniline (1 mol) with MeI (3 mols) and KOH (2 mols) dissolved in water (Pawlinoff, J R 13, 448, Bl[2] 37, 493) Plates (from a cohol) Converted by moist Ag,O into C.H.,NMe,OH a deliquescent, crystalline, caustic ase When the methylo nodide is distilled it splits up into NMe2Ph and MeI, but these recombine in the receiver however, a current of HCl be passed through the retort NMe, PhHCl condenses in the receiver, while MeI escapes and may be condensed in a second colder receiver (Merill, J pr [2] 17, 286) When treated in a sealed tube with a solution of potassium in anhydrous liquefied ammonia it yields KI, NMe, and possibly benzene (Thompson a Cundall, C J 53, 761) Boiling conc KOHAq slowly decomposes PhNMe, I into di methylaniline, KI, and MeOH (Claus a Rauten berg, B 14, 621) The methylo iodide gives rise to the following derivatives -PhNMe₃I₃ [115°] Brown trimetric plates (Geuther, A 240, 69) PhNMe₃I₄ [87°] (Dafert, M 4, 500) Lustious green monoclinic needles, $a \ b \ c = 179411251$, $B = 69^{\circ}$ 43' — PhNMe₃I, [65°] Violet black Trimetric crystals plates - PhNMe, IZnI. (Hjortdahl) — PhNMe, ClHgCl₂ [188°] S 36 at 62° Needles (Hubner, A 224, 352) — (PhNMe,Cl)₂PtCl₆ Orange needles (from water) S 33 at 7 4° - (PhNMe₃)₂Cr₂O, Prisms S 5 -(PhN Me,)2Cr,O10 Monoclinic crystals (Hjort

Ethylo rodide B'Etl [125°] Identical with methyl ethyl aniline methylo iodide, KOH splits off dimethylaniline (Claus a Howitz, B 17,1325) —PhNMe,EtI, [81°] Dark violethexagonal rhombohedra (Geuther) -PhNMe,EtI, Lustrous bluish - green plates -[45°] PhNMe EtI Violet black plates

References — Brono , Brono di - Nitro , Chloro , Chloro Nitro , Iodo di -, Nitro , and NITROSO DI METHYLANILINE

DIMETHYLANILINE - AZYLINE v methyl-amulo benzene Azo-dimethylaniline

DI - METHYL - ANILINE -PHTHALEIN v

TETRA METHYL DI AMIDO DI PHENYL PHTHALIDE METHYLANILINE SULPHONIC ACID v. METHYLAMIDOBENZENE SULPHONIC ACID

o DIMETHYLANISIDINE v AMIDO PHENOL.

METHYL-ANISOL is the methyl ether of CRESOL

(B 1) METHYL-ANTHRACENE O,H, te. $C_{\bullet}H_{\bullet}Me\begin{bmatrix} 6\\ 5 \end{bmatrix}$ Mol w 192 [208°]

(Börnstein), [200°] (Birukoff) Formed by distilling erythro-oxy methyl anthraquinone with zinc dust (Birukoff, B 20, 2070) Formed also by boiling iso methylanthraquinone with zinc dust and ammonia, and splitting off water from the resulting methyl hydroxanthranol by boiling with xylene (Börnstein, B 15, 1821) plates—B'C₂H₂(NO₂)₃OH red needles Gives on oxidation methyl-anthraquinone [167°] and

the corresponding anthraquinone carboxylic acid. Forms a di bromo methyl anthracene [148°]

Hexahydride C₁₅H₁₆. [c 65°] Formed by reducing the dilactone of benzophenone dicarboxylic acid with phosphorus and hydric iodide (Graebe a Juillard, A 242, 256) Plates V sol alcohol, ether, and chloroform through a red hot tube it yields a hydrocarbon [195°] On oxidation it yields methylanthraquinone [154°]

(B 2) Methyl-anthracene

coal tar oil, and hence is present in crude anthracene and phenanthrene (Japp a Schultz, B 10, 1049)

Formation -1 By passing di-tolyl methane through a red hot tube (Weiler, B 7, 1181) -2 By passing di tolyl ethane through a red hot tube (O Fischer, B 7, 1191, 8, 675) -3 Apparently occurs among the products obtained by passing vapour of oil of turpentine through a red-hot tube (Schultz, B 10, 84)—4 By the action of zinc dust at high temperatures on chrysophanic acid C₁₅H₆O₂(OH)₂, on emodin C₁₄H₆O₂(OH)₈ (Liebermann, B 8, 970, A 183, 183) 163), on aloin (in small quantity) (E Schmidt, B 8, 1275, Ar Ph [3] 8, 496), on the acid [4 1] CH, C, H, CO C, H, CO, H (Gresly, A 234, 238), on abietic acid (colophony), on gum benzoin (Ciamician, B 11, 273), on chrysarobin (Liebermann a Seidler, A 212, 34), and on methyl quini zarın (Nietzki, B 10, 2013) — 5 Byboiling phenyl xylyl ketone C₆H₅ CO C₆H₂Me₂[1 2 4] for a long time (Elbs, J pr [2] 35, 472) The isomeric CaH, CO CaH, Me [1 2 5] condenses on boiling to the extent of 10 to 20 pc to (B 2) methyl anthracene, dehydrating agents either stop the reaction or split off benzoic acid

Properties —Yellowish plates (from alcohol) Sublimes in large white plates, exhibiting blue **fl**uorescen**c**e Sl sol alcohol, ether, and HOAc, v sol CHCl3, benzene, and CS2 Chromic acid in HOAc oxidises it to anthraquinone carboxylic acid [282°] Conc HNO, added to its alcoholic solution forms methyl anthraquinone Bromine in CS₂ forms a di bromo derivative [156°] (Fischer), which yields, on further bromination, a tetra bromo derivative crystallising from toluene in needles The picric acid compound melts at [93°] (Gresly)

Di-methyl-anthracene CieH14 s.c.

One of the products obtained by passing benzyl mesitylene through a red hot tube parated from the di methyl anthracene [218°] which accompanies it in smaller quantity, by crystallisation from toluene, in which the compound, melting at 71°, is extremely soluble Further purified by means of its picric acid compound (Louise, Bl [2] 44, 180, A Ch [6] 6, 191) White needles, v e sol cold benzene and toluene, m sol HOAc and alcohol On oxidation with CrO, in HOAc it yields di methylanthraquinone [158] The picric acid compound forms long red needles. Forms a grey compound with nitro anthracene.

[219°] One of the products of the passage of benzyl-mesitylenethrough a red hot tube (Louise, Bl [2] 44, 178) Rhomboidal plates, insol cold alcohol, sl sol ether, ligroin, and acetic acid, v sol hot benzene and toluene Forms small colourless leaflets when sublimed Br in CS2 forms a crystallised bromo-derivative The picric acid compound crystallises in red CrO, in HOAc oxidises it to a dimethyl anthraquinone [170°] Forms a green compound with nitro-anthracene

Di methyl-anthracene

$$C_6H_*$$
 C_6H_*
 C

Obtained by distilling with zinc dust the tri-oxy- \mathbf{d}_{1} methyl-anthraquinone derived from m xylene carboxylic acid, gallic acid, and H2SO4 (Birukoff, B 20, 871) Plates Oxidised by CrO, to a dimethyl-anthraquinone [112°]

D1-methyl-anthracene
$$C_0H_1$$
 $C_0H_2Me_2$

[216°] Obtained by treating a mixture of toluene (3 pts), CS₂ (3 pts), and chloroform (1 pt) with AlCl_s (2 pts) (Elbs a Wittich, B 18, 348) chromic acid it gives a quinone [162°] Probably identical with the isomeride [219°]

[203°] From [2 4 1]C,H₃Me₂ CO C,H₄ CO₂H[1 2] by heating with red hot zinc-dust (Gresly, A 234, 238) Plates Possibly identical with the 180meride [220°-226°]

Di-methyl-anthracene

$$C_eH_*$$
 $\begin{bmatrix} CH \\ I \end{bmatrix}$ $C_eH_2Me_2\begin{bmatrix} 1 & 3 \\ 6 & 4 \end{bmatrix}$ [246°] Formed by

reduction of di-methyl-anthraquinone [183°] with zinc-dust and NH, White plates, with bluish-green fluorescence Its picrate forms garnet-red needles, decomposed by alcohol (Elbs a Eurich, B 20, 1363)

Di-methyl-anthracene

coal tar xylene by chlorination at boiling temperature, and subsequently heating the resulting [3 1]C₆H₄(CH₃)(CH₂Cl) with water at 210° (Van Dorp, B 5, 674) White fluorescent plates Yields on oxidation with chromic acid a quinone [153°] Br gives a di bromo di-methyl anthracene [154°] Perhaps identical with the following isomeride

Di-methyl-anthracene

$$C_6H_3Me$$
 C_6H_4Me
 C_6H_4Me
 C_8H_4Me
 C_8H_4Me

Occurs in coal-tar (Zincke a Wachendorff, B 10, 1481) Formed from toluena, AlCl, and acetylene tetra-bromide (Anschütz, A 235, 172) Prepared by acting on toluene with methylene chloride in presence of AlCl, (Friedel a Crafts, Bl. [2] 41, 323, A Ch [6] 11, 266). Scales With CrO, in HOAc it gives dimethylanthraquinone [160°], which forms an orange

solution in H2SO4 The picric soid com pound crystallises in slender needles

Di-methyl-anthrasene

methyl anthragene dihydride.

C_eH₃Me<CHMe>C_eH₃Me by distillation over red hot zinc dust (Anschutz, A 235, 320), Greenish-yellow laminæ (from benzene), m sol benzene, sl sol alcohol Gives on oxidation di methyl-anthraquinone [23 6°

s Di methyl-anthracene dihydride CisHis v.c. C₆H₄<CMeH C_{CMeH} C₆H₄ [181°] From ethylidene bromide, benzene, and AlCl, (Anschutz, A 235, 305) Yellow laminæ (from alcohol) Sublimes in yellow needles V sol benzene, CS2, and ether, sl sol cold alcohol and glacial HOAc Distillation over red hot zinc dust gives anthra cene Oxidation gives anthraquinone Bromine in HOAc gives C₆H₄<CMeBr C₆H₄, which crys tallises from toluene in needles

Picrate C₁₆H₁₆C₆H₂(NO₂)₃OH [174°] u-Di-methyl anthracene dihydride

C_sH₄ CH₂ C_sH₄ [56°] Formed by the action of HI and red phosphorus on dimethylanthron $C_6H_4 < \stackrel{CO}{<} C_6H_4$ at 150° (Hallgarten, B 21, 2508) White crystals, sol ether, benzene, and HOAc

 $\begin{bmatrix} 1 \\ 6 \end{bmatrix} 2 3 5$ [236°] (W), [243°] (G) Obtained by distilling '\$\psi\$ cumene phthaloylic' acid C.H. Me, CO C.H. CO H with zinc dust (Gresly, A 234, 239) Formed also by distilling tri oxy di methyl anthraquinone [244°] over zinc dust (Wende, B 20, 868) Exhibits green fluores

Tri-methyl-anthracene
$$C_1, H_{10}$$
 is $\begin{bmatrix} 2 & 5 & 1 \\ 1 & 6 \end{bmatrix}$ $C_0H_2Me_2$ $\begin{bmatrix} CH \\ CH \end{bmatrix}$ C_0H_3Me $\begin{bmatrix} 1 & 3 \\ 6 & 3 \end{bmatrix}$ $\begin{bmatrix} 2279 \\ 1 & 6 \end{bmatrix}$

Formed by boiling di p xylyl ketone $C_8H_2Me_2$ CO $C_6H_3Me_2$ for six hours, H O being eliminated Colourless plates, with bluish green fluorescence Sublimes below 100°, slightly volatile with alcohol V sl sol cold alcohol, v sol ether By CrO, and acetic acid it is oxidised to tri methyl anthraquinone [184°] (Elbs a Olberg, B 19, 409, J pr [2] 35, 483)
Tetra-methyl-anthracene C₁₈H₁₈ [c 280°]

A small quantity (3 g) is formed from m xylene (100 g), Al_2Cl_8 , and acetylene tetrabromide (Anschutz, A 235, 173) CrO₂ gives a substance (tetra methyl anthraquinone?) which forms needles [c 300°]

Tetra methyl-anthracene (?) [280°] From o-xylene, Al₂Cl₂, and acetylene tetrabromide (Anschütz, A 235, 175) Fluorescent needles

Tetra-methyl anthracene (?) [280°] Formed similarly from p xylene (A)

Tetra-methyl-anthracene C14H6Me4. [163°]. Formed by the action of methylene chloride in presence of AlCl, on m-xylene, and in smaller

quantity on ψ -cumene (Friedel a Crafts, A Ch [6] 11, 268) Crystallises from benzene Gives a dark red crystalline compound with picric acid Conc H2SO4 gives a yellow solution CrO2 in HOAc oxidises it to tetra methyl anthraquinone [206°]

Tetra-methyl-anthracene dibromide

C₆H,MeCBrMeC₆H₂Me From the corresponding tetra methyl anthracene dihydride by bromination (Anschutz, A 235, 321) Yellow needles, decomposes when heated Tetra methyl-anthracene dihydride

[171°] Obtained by the action of ethylidene chloride on toluene in presence of Al₂Cl₂ (Anschutz, A 235, 317) Pale yellow trimetric laminæ, $a \ b \ c = 675 \ 1 \ 924$ (from alcohol and HOAc), v sol benzene, sl sol HOAc, v sl sol alcohol Distillation over red hot zinc dust gives di methyl anthracene Oxidation gives di - methyl - anthraquinone [236°]

Picrate C₁₈H₂₀C₅H (NO₂)₂OH [165°] Red

glistening needles

Hexa-methyl-anthracene C14H4Me [c 220°] One of the products of the action of methylene chloride on \psi cumene in presence of AlCl3 (Friedel a Crafts, A Ch [6] 11, 272) Not vola tile at 410° The alcoholic solution gives with pieric acid a brownish black pp [203°] Conc H,SO, forms a red solution, becoming colourless after absorbing moisture

References - DI BROMO METHYL-ANTHRACENE and Amido methyl anthracene dihydride and DIBROMIDE

DI-METHYL-ANTHRACHRYSONE v TETRA OXY DI METHYL-ANTHRAQUINONE

DI METHYL ANTHRACYL AMINE . MFTHY! ANTHRAMINE

DI-METHYL ANTHRAFLAVIC ACID v DI-

OXY DI METHYL ANTHRAQUINONE

METHYL ANTHRAGALLOLS v (1 2 3) Tri-OXY MI THYL ANTHRAQUINONES

DI METHYL ANTHRAMINA
Di methyl anthracylamine [155°] Formed by heating the methylo hydrate Thin golden plates Soluble in alcohol with a green fluor

Salts -B HCl colourless plates, decomposed by water —B' H Cl.PtCl, yellow pp

[215° uncor] Methylo rodide B'Mel Formed by heating anthramine with methyl iodide at 100° Flat needles, sol hot water, sl sol cold, nearly insol alcohol

Methylo chloride platinum salt

B'2Me Cl.PtCl, yellow crystalline pp Methylo hydrate B'Me(OH) strongly alkaline Formed by the action of Ag.O on the iodide, on boiling the aqueous solution it decomposes into di methyl anthramine and methyl alcohol (Bollert, B 16, 1636)

METHYL-ANTHRANILIC ACID & AMIDO-

TOLUIC ACID

(B 1) METHYL-ANTHRAQUINONE (B 1) METHYL-ANTHRAGUINOUS

C₁₈H₁₀O₂ is C₀H₄CO_OC₀H₂Me [6 1] Mol

w 222 [154°] (Graebe), [167°] (Birukoff), [24 1]C₀H₁Me₂CO C₀H₁CO₂H[1 2] with conc [176°] (Börnstein) Formed by oxidising (B 1)-methyl-anthracene with CrO₂ and HOAc (Birukoff), [24 1]C₀H₂Me₂CO C₀H₂CO₂H[1 2] with conc methyl-anthracene with CrO₂ and HOAc (Birukoff), H₂SO₄, the yield is 60 to 70 pc of the theoretical (Gresly, A. 234, 240, Elbs a Gunther, koff, B 20, 2070) Formed also by oxidising B, 20, 1364) Small needles, al sol benzene Vol. III

(B 1) methyl anthracene hexahydride (Graebe A 242, 256) The same, or the following, methyl anthraquinone is a by product in the preparation of anthraquinone (Wachendorff a Zincke, B 10, 1485, Börnstein, B 15, 1820) Small needles (from dilute HOAc) V. e sol alcohol and benzene

(B 2) Methyl-anthraquinone

 $C_{e}H_{*} < \stackrel{CO}{<_{CO}} > C_{e}H_{*}Me \begin{bmatrix} 6 & 2 \end{bmatrix}$ [163°] (F), [172°] (E), [177°] (Römer a Link, B 16, 695)

Formation -1 By warming an alcoholic solution of (B 2) methyl anthracene with nitric acid, ppg with water, and subliming (O Fischer, B 8, 675)—2 In small quantity by boiling phenyl m xylyl ketone (Elbs, J pr [2] 35, 471)
3 By warming [4 1]CH, C,H, CO C H, CO₂H with H,SO, at 170° for ten minutes (Gresly, A 234, 239)

Properties — Yellow needles Sublimes in almost colourless needles V sol alcohol, benz ene, and HOAc (R a L), according to Fischer, however, it is al sol these solvents. Conc H SO, forms a blood red solution which becomes When heated with zinc-dust violet on heating it yields methyl anthracene [203°] With fuming HSO, it yields a disulphonic acid, which on fusion with potash forms di oxy methyl anthra quinone (methyl alizarin) [252°] (Fischer)

Isomeride of Methyl anthraquinone

METHANTHRENE

Di methyl-anthraquinone C₁₀H₁O₂ $C_6H_4 < \stackrel{CO}{<} C_0 + H_2Me_2 \begin{bmatrix} 1 \\ 6 \end{bmatrix} ? [158]$ Obtained by oxidising the corresponding dimethyl an thracene [71°] Formed also by heating benzoyl mesitylenic acid C₆H₃ CO C₈HMe.CO H with P.O., and subliming the product (Louise, A Ch [6] 6, 193, 228, Bl [2] 11, 181) Yellow acıcular prisms (from chloroform acetone) or needles (by sublimation) Insol water, sl sol alcohol, sol With zinc-dust and chloroform and acetone KOH it gives an intense red colour This di methyl anthraquinone ought theoretically to be identical with those melting at 180 and 112° (v

Di methyl anthraquinone C₁₆H₁,O₂. [170°] Obtained by oxidising di methyl anthiacene [219°] with CrO, in HOAc (Louise, A Ch [6] 6, 189, Bl [2] 44, 180) Yellow needles (from 189, Bl [2] 44, 180) Yellow needles (from alcohol) With zinc dust and KOH it gives a characteristic red tint, which disappears en heating

Di methyl anthraquinone

$$C_{\bullet}H_{\bullet} < \stackrel{CO}{<} C_{\bullet}H_{\bullet}Me \begin{bmatrix} 1 & 3 & 4 \end{bmatrix}$$
 [183°]

Obtained by heating oxylyl phenyl ketone carboxylic acid (oxyloyl obenzoic acid) [3 4 1] C, H, Me, CO C, H, CO, H[1 2] with conc. H₂SO₄ By HNO₅ (S G 1 2) at 220° it is oxi dised to anthraquinone di carboxylic acid [340°] (Elbs a Eurich, B 20, 1361).

Di-methyl-anthraquinone

$$C_{e}H_{e} < \frac{CO}{CO} > C_{e}H_{e}Me_{e} \left[\frac{1}{6} 24 \right]$$
. [180°].

and alcohol By dil HNO, it is oxidised to anthiaquinone m di carboxylic acid [above 330°] Reduced by zinc dust and ammonia to a hydrocarbon [85°] which forms with pieric acid reddish-brown scales [135°]

Di methyl anthraquinone

C₆H₄CO C₆H₂Me₂[$\frac{1}{6}$ 25] [118°] Formed by warming [4 1 x]C₆H₃Me₂ CO C₆H₄ CO₂H[2 1] with cone H₂SO₄ at 120° (Gresly, A 234, 240) Di methyl anthraquinone

 $C_eH_e < CO_o > C_eH_2Me_2 \begin{bmatrix} 1 \\ 6 \\ 2 \\ 4 \end{bmatrix}$? [112°] Obtained by oxidising the di methyl anthracene [220°–226°] (Birukoff, B 20, 871)

Di methyl-anthraquinone

 C_0H_* $\stackrel{CO}{CO}$ $C_0H_2Me_2$ [162°] Obtained by oxidising di methyl anthracene [216°] (Elbs a Wittich, B 18, 348)

Di-methyl anthraquinone

C_oH_sMe CO C_oH_sMe [236°] Formed by oxidation of di methyl anthracene [244°] Pale yellow needles, si sol HOAc, v si sol alcohol (Anschutz, A 235, 321)

Di-methyl-anthraquinone

 $C_oH_sMe < \stackrel{CO}{CO} > C_oH_sMe$ [155°] Obtained by oxidising the di methyl anthracene occurring in coal tar xylene (Wachendorff a Zincke, B 10, 1482) Small light yellow needles (from dilute alcohol) May be sublimed M sol alcohol, ether, and HOAc

D1-methyl-anthraquinone

 $C_eH_3Me < \stackrel{CO}{CO} > C_eH_3Me$ [160°] Obtained by oxidising the di-methyl anthracene formed from toluene, methylene chloride, and AlCl₃ (Friedel a Crafts, A Ch [6] 11, 266) Forms an orange solution in H_2SO_4 Probably identical with the preceding

Tri-methyl anthraquinone

C₆H₄CO_{CO}C₆HMe₄ [Me Me Me = 1 2 4] [161°] Formed by warming ψ cuminoyl benzoic acid C₆H Me₄CO C₆H₄CO₂H for a short time with cone H₂SO₄ (Gresly, A 234, 240) Needles

Tri-methyl-anthraquinone

 $\begin{bmatrix} 2 \ 5 \ 6 \end{bmatrix} C_6 H_2 Me_2 < \begin{matrix} CO \\ CO \end{matrix} > C_6 H_3 Me \begin{bmatrix} 1 \ 6 \ 3 \end{bmatrix}$ [184°] Formed by oxidation of the tri methyl anthra cene obtained from di p xylyl ketone (Elbs a Olberg, B 19, 409)

References — Amido-, Nitro, and Oxy-METHYL ANTHRAQUINONES

METHYL ANTHRAQUINONE CARBOXY. LICACID $C_{16}H_{16}O_4$? & $C_9H_3Me < {}^{CO}_{CO} > C_8H_3$ CO_2H

[246°] Occurs among the products of the oxidation of coal tar di-methyl anthracene by CrO. in HOAc (Wachendorff a Zincke, B 10, 1483) Small needles (by sublimation); v. sol. hot alcohol

D1-methyl-anthraquinone carboxylic acid C₁,H₁,O₄, c C₂H₄,CO_CO C₂H₂Me₂ CO₂H [240°] Formed by heating ψ-cuminoyl-benzoic acid C₂H₂Me₂ CO C₂H₄ CO₂H[2 1] with fuming H₂SO₄ (Gresly, A. 234, 241). Small needles. V. sol.

alkalıs, al. sol alcohol and benzene May be sublimed

DI-METHYL-ANTHRARUFIN v DI OXY DI-METHYL ANTHRAQUINONE

DI-METHYL-ANTHRONE C₁₆H₁₄O t.c. C₆H₄CO_CCMe₂C₆H₄ [94°] Formed by the action of MeI and KOHAq on anthranol (Hallgarten, B 21, 2508) Transparent crystals, v sol benzene, ether, sl sol petroleum ether Converted by the action of HI and red phosphorus into di methyl anthracene dihydride

METHYL-ARBUTIN v' Arbutin

METHYL ARSENATE Me, AsO, (214°) S G 14 1 559 Formed from Ag, AsO, and MeI (Crafts, Bl [2] 14, 99)

METHYL ARSENITE Me, AsO, (129°) SG 1428 VD 601. From AsCl, and NaOMe (Crafts, Bl [2] 14, 104) When arsenious acid is dissolved in aqueous NaOH and treated with alcoholic MeI the product is not mono methyl arsenite but methane arsonic acid CH₃ AsO(OH)₂ (Klinger, A 249, 149, cf vol 1 p 317)

METHYL ARSINE v Organic Arsenic compounds

METHYL-ATROLACTIC ACID v OAY TOLYL-PROPIONIC ACID

METHYL-ATROPIC ACID v PHENYL CRO
TONIC ACID

METHYL-AURIN C₂₀H₁₀O₄ aq A by product in the preparation of aurin (Zulkowsky, A 194, 131, 202, 210, M 3, 476) Brick red crystals with green lustre (from 60 pc alcohol) Its al coholic solution is yellowish red, and becomes crimson on addition of alkalis It loses aq at 100°, but does not melt below 200° HCl added to its dilute alcoholic solution ppts C₂₃H₂₅ClO₄ as red crystals with blue reflex On heating with water in sealed tubes at 245° methyl aurin is split up into p cresol and di oxy benzo phenone Alkaline KMnO₄ oxidises methyl aurin to C₁₆H₁₄O₄ Potash fusion forms p oxybenzoic acid Zinc dust and HOAc reduce it to methyl leucaurin C₂₀H₁₆O₄, which crystallises in long colourless needles H,SO₄ forms red crystals of (C₀H₁₆O₃) H₂SO₄ which are blue by reflected light Bromine in HOAc forms crystals of C₂₆H₁₂Br₄O₄HBr aq, which have a steel blue reflex

METHYL-AZELAIC ACID v OCTANE DI CARBOXYLIC ACID

METHYL DIAZO- COMPOUNDS v $D\iota$ Azo compounds

TETRA-METHYL TETRAZONE $C_4H_{12}N_4$ to $(CH_3)_2N$ N N N(CH₃). (130°) Prepared by the oxidation of dimethyl hydrazine in ethereal solution with HgO (Renouf, B 13, 2173) Oily fluid Explodes with violence if heated above 130° Alkaline in reaction Reduces AgNO₃ to a silver mirror It is decomposed by boiling aqueous acids into dimethylamine, methylamine, formic acid, and nitrogen

Salts — The picrate B'C₆H₂(NO₂)₂OH forms yellow prisms V sol water, sl sol alcohol. The other salts are also easily soluble in water

METHYL-250-BARBITURIC ACID C₅H₄N₂O₅. Formed by treating intro methyl-uracil

CO NMe CH CO NO2 with tin and HCl (Lehmann, A 253, 80) Needles, v sol cold water.

Di-methyl barbituric acid v Di methyl derivative of BARBITUBIC ACID, vol 1 p 439

METHYL BENZAMIDES v Benzoyl derivatives of METHYLAMINES

METHYL-BENZENE v TOLUENB

Di methyl-benzene v Xylene

Tri-methyl-benzenev & Cumene, Mesitylene, and Hemimellithene

Tetra-methyl benz ne v Durene

Penta-methyl benzene C₁₁H_{1e} ie C_eHMe, Mol w 148 [52°] (231° 1 V) V D 5 27 (calc 5 12) H F 31,900 H C 1,554,100 (Stohmann, Kleber, a Langbein, J pr [2] 40, 83) One of the products of the action of MeCl on benzene or toluene in presence of AlCl, (Friedel a Crafts, A Ch [6] 1, 472, Ador a Rilliet, B 12, 332) bormed also in like manner by the action of MeCl and AlCl, on tri methyl benzenes at 100°- 110° , the fraction (220°-235°) on crystallisation from alcohol deposits C_6Me_6 first, and the pentamethyl benzene remaining in the mother liquor may then be purified by means of its sulphamide (Jacobsen, B 20, 896) Penta methyl benzene is a by product in the formation of tetramethylbenzene by the action of MeI and AlCl, on ψ cumene (Claus, J pr [2] 38, 231)

Properties —Flat prisms, v e sol alcohol Reactions — 1 Bromine in CHCl, forms C. Me. Br $[163^\circ]$ (292° 1 V) (F a C , Jacobsen, B 20, 898) -2 AgNO, and vapour of Br forms dı bromo c durene [202°] (Gottschalk, B 20, 3288) —3 CISO,H forms the sulphone and sulphochloride (Jacobsen) -4 Cold conc H2SO4 does not form the corresponding sulphonic acid, but yields c tetra methyl benzene sulphonic acid and hexa methyl benzene (J) -5 KMnO, forms benzene penta carboxylic acid (F a C) —6 Fum ing nitric acid forms di nitro c tetra methyl benzene [178°] (Gottschalk, B 20, 3287) Dilute nitric acid acting on its solution in benzene produces tetra methyl benzoic acid [165°] -7 Heat ing with AlCl, forms isodurene, C₆Me₆, and other hydrocarbons (Jacobsen, B 18, 340) — 8 Cl CONH₂ and AlCl, convert C₆HMe₅ dissolved in CS, into the amide of penta-methyl benzoic acid (Jacobsen, B 22, 1219)

Picric acid compound $C_6HMe_3C_6H_2(NO_2)_3OH$ [131°] Golden yellow

Hexa methyl-benzene $C_{12}H_{16}$ i.e. $C_{0}Me_{0}$ Mol w 162 $[164^{\circ}]$ (F a C), $[166^{\circ}]$ (J) (264°) S (95 pc alcohol) 2 at 0° V D 5 73 $(calc\ 5\ 61)$ (Fa C), $5\ 58$ (H) H C v 1,709,600 H C p 1,712,200 H F 36,800 (Stohmann, Kleber,

a Langbein, J pr [2] 40, 84)
Formation -1 The final product of the action of McCl on benzene or toluene in the presence of AlCl, (Friedel a Crafts, A Ch [6] 1, 467, C R 91, 257, Ador a Rilliet, B 12, 332) -2 From o-di chloro benzene, MeCl, and AlCl, at 100° (Friedel a Crafts, A Ch [6] 10, 411) — 3 A by product in the formation of (1,2,3,4)-tetra methyl benzene by the action of MeI and AlCl, on ψ cumene (Claus, J pr [2] 38, 231) 4 By heating dimethylaniline methylo-iodide at 330° (Hofmann, B 5,721) —5 Said to be a product of the action of fused ZnCl, on sugar (C. J. 38, 863, D P. J 237, 146) —6 Formed as a

by product in the preparation of cumidine by heating xylidine hydrochloride with methyl alcohol, also in small quantity by the action of methyl alcohol at a high temperature on aniline hydrochloride (Hofmann, B 13, 1729) -7 By dropping methyl alcohol upon strongly-heated ZnCl₂ (Le Bel a Greene, Am 2, 21) —8 By pouring acetone upon fused ZnCl₂ (H Greene, C R 87, 931) —9 By shaking crotonylene CMe CMe with H2SO4 (3 pts.) diluted with water (1 pt) (Favorsky, J pr [2] 37, 384, Lwoff a Almedingen, Bl [2] 37, 493)—10 Together with other products by the prolonged action of conc H.SO, upon durene (Jacobsen, B 19, 1211)—11 A product of the action of cold conc H.SO, on penta methyl benzene (Jacobsen, B 20, 901)

Properties - Colourless plates (from alcohol) or prisms (from benzene), insol water, sl sol cold, v sol hot, alcohol, v sol benzene Forms iridescent plates on sublimation Does not dis

solve in conc H₂SO₄

Reactions — 1 Bromine at 100° yields

C₁:H₁:Br₄ [255°] (F a C), [227°] (H) —

2 KMnO₄ oxidises it at a low temperature to mellitic acid -3 Dilute mtric acid yields c tetramethyl benzene dicarboxylic acid (Jacobsen, B 22, 1216) -4 When heated with AlCl, at 200° a gas is given off and penta methyl benzene, durene (Friedel a Crafts, C R 100, 692), isodurene, tri methyl benzenes, xylenes, toluene, and benzene are formed (Jacobsen, B 18, 339) -5 PCl, forms hexa chloro hexa methyl-benzene $(q \ v)$

Picric acid compound

C₆Me₆C₆H₂(NO₆),OH [169°] Golden plates METHYL BENZENE CARBOXYLIC ACID vTOLUIC ACID

Di methyl-benzene carboxylic acid o MESITYLENIC and DI METHYL BENZOIC ACIDS

Tri - methyl - benzene carboxylic acid c. **♦ CUMINIC ACID**

Methyl-benzene dicarboxylic acid v Uvitic ACID, METHYL ISOPHTHALIC ACID, METHYL TEREPH-THALIC ACID, and TOLUENE DICARBOXYLIC ACID

Di-methyl-benzene dicarboxylic acid v Di-METHYL-ISOPHTHALIC and DI METHYL-TEREPH-THALIC ACIDS

Tri-methyl-benzene dicarboxylic acid C.HMe,(CO,H), Obtained by oxidising C.HMe, CO C.H, with KMnO, in alkaline solution (Ador a Meyer, J 1879, 562) Needles (fromwater)—BaA"aq Slender needles, almost insol water

Tetra-methyl-benzene dicarboxylic acid C₆Me₄(CO₂H)₂ [6 5 4 3 2 1] [249°] Formed by boiling C₆Me₆ with dilute HNO₅ (Jacobsen, B 22, 1215) Small needles (from hot water) or prisms (from alcohol) Yields c durene when distilled with lime -BaA', 2aq

DI-METHYL-BENZENE GLYCOL v Dr-w-OXY XYLENE

METHYL-BENZENE SULPHINIC ACID v. TOLUENE SULPHINIC ACID

Tri-methyl-benzene sulphinic acid C.H.Me. (SO.H) [1:8 4.6] [98°] Long needles (from water) —NaA' —BaA'. S 5 at 7°. Thin plates —AgA' (Badloff, B. 11, 82)

METHYL-BENZENE SULPHONIC ACID . TOLUMNE SULPHONIC ACID.

Di methyl-benzene sulphonic acid v XYLENE SULPHONIC ACID

c-Tri-methyl benzene sulphonic acid

C₆H₂Me₃(SO₃H) [1 2 3 5] Hemmellithene sul-phonic acid Formed by sulphonation of hemimelli hene (Jacobsen, B 15, 1858, 19, 2517) Crystallises from dilute H2SO4 in six sided plates or tables (containing aq) -NaA'aq tables, v sol hot, m sol cold, water - *BaA'2 brittle plates, v sl sol water

Amide C.H.Me,SO2NH2 [196°] Prisms or needles Less soluble in alcohol than the amide of ψ -cumene sulphonic acid

Isomerides v ψ -Cumene sulphonic acid and MESITYLENE SULPHONIC ACID

Tetra methyl-benzene sulphonic acid v. DURENE SULPHONIC ACID

Penta-methyl-benzene sulphonic acid C.Me.SO.H Obtained by treating penta methylbenzene with ClSO₃H and treating the product with NaOH to convert the C.Me.SO.Cl first formed into C₆Me₃SO₃Na (Jacobsen, B 20, 899) In the action of CISO, H on C, Me, H a sulphone [98 5°], crystallising from petroleum ether in needles, is also formed The free acid, liberated by shaking the sodium salt with light petroleum and H2SO4, at once undergoes hydrolysis, C.HMe, dissolving in the petroleum

Salts -A'Na tables (from neutral aqueous solution) or plates (from hot, dilute, NaOH), sl sol cold water, m sol hot water, insol cold, dilute NaOH —A'K plates (from hot water) —A'aBa A'Ag plates, v sl sol cold, m sol hot, water - A', Cu greenish white tables sl sol water plates, v sl sol hot water -A'2Ca plates

A'₂Cu greenish white tables, sl sol water

Chloride [82°] Plates (from EtOH), or
prisms (from Et₂O), v sol EtOH and Et₂O

Amide [186°] Prisms, v e sol hot, m

sol cold, EtOH, insol water KMnO, produces a sulphamic acid [c 265°]

METHYL - BENZGLYCOCYAMIDINE BENZCREATININE

METHYL-BENZGLYCOCYAMINE # BENZ-CREATIN

TETRA METHYL BENZIDINE v. TETRA-METHYL-DI-P AMIDO DIPHENYL

METHYL-BENZIL v PHENYL TOLYL DIKE-AONE

METHYL-BENZOIC ACID v TOLUIC ACID Di-methyl-benzoic acid C₂H₁₀O₂ v.e

C_eH_sMe₂ CO H [6 2 1] m-Xylene c-carboxylic acid [97°-99°] Formed by fusing potassium m xylene c-sulphonate with sodium formate (Jacobsen, B 11, 21) Short needles (from water) Forms m-xylene when distilled with

D1-methyl-benzoic acid

 $H_{2}Me_{2}CO_{2}H$ [4 2 1] m Xylens i carboxylic acid Xylylic acid Xylorc acrd [126°]. (267°) at 727 mm

Formation.—1 By the oxidation of ψ -cumene by dilute nitric acid, being separated from the accompanying C₀H₃Me₂CO₂H [5 2 1] through the greater solubility of its Ca salt Fittig a Laubinger, A 151, 269) -2 By treating bromom xylene with sodium and OO2 (Kekulé, A 187, 186) -3 By warming its nitrile with H.SO. (85 pc) and heating the resulting amide with cone HClAq at 170° (Birukoff, B 20, 871, A \$40. 286) -4. By heating its diphenylamide

with HClAq (v infra) -5 By decomposing its chloride (v infra) with water

Properties - Slender needles (from water) or monoclinic prisms (from alcohol) May be sublimed Almost insol co'd water, sl sol hot water, v sol hot alcohol Gives m xylene when Chromic acid mixture oxiheated with lime dises it to $C_6H_3Me(CO_2H)_2$ [3 1 4]

Salts —CaA', 2aq monoclinic prisms, ▼ sol water —BaA', 8aq ?—AgA'

Chlorade C, H, Me, COCI [25 5°] Formed by passing COCl₂ into m xylene containing AlCl₃, and heating to 100° (Ador a Meyer, B 12, 1968)

Amide C.H.Me. CONH [180°] Formed by warming the nitrile with H.SO. (85 pc) Formed also by the action of NH, COCl on m xylene in presence of AlCl, (Gattermann, 244, 53) Formed also by passing gaseous HCNO and HCl gas into m xylene containing AlCl, on the water bath (Gattermann a Rossolymo, B 23, 1196) Long shining needles (from water) Almost insol cold water, v sol alcohol

Anilide C.H.Me CONHPh [138 5°] Crys-

tals, v sl sol hot water

Diphenylamide C. H. Me, CONPh, [142°] Formed from m xylene and NPh, COCl in pre sence of AlCl, (Lellmann a Bonhöffer, B 20, Monoclinic crystals, v e sol hot alco hol, HOAc, and chloroform, sl sol hot ether, v sl sol hot petroleum ether

[25°] Nitrile C₆H₃Me₂CN (221°) 18 9871 (Hinrichsen, B 21, 3082) VD 464. Formation -1 By heating the formyl deri vative of m-xylidine with zinc-dust, the yield being about 12 pc (Gasiolovsky a Merz, B 18, 1012) -2 By distilling the corresponding PO(OC,H3Me,), with KCy, the yield being 15 p c (Kreysler, B 18, 1713) -3 From m xvli dine by Sandmeyer's reaction (Birukoff B871) Properties - Triclinic crystals (from dilute alcohol) Volatile with steam Yields benzyl di methyl amine on reduction

Amidoxim C₆H₃Me₂C(NH₂) NOH [178°] Xylenyl-amidoxim Formed by the action of hydroxylamine on the nitrile at 85° (E Oppen heimer, B 22, 2443) White needles, v sol alcohol, ether, chloroform, and hot water, sl sol cold water Reactions -1 Etlacting on its Na. derivative forms CoH3Me C(NH) NOEt which crystallises in white needles, [172°], v sol alco hol, ether, chloroform, benzene, and boiling water, sl sol cold water Excess of HCl converts the ethyl derivative into C,H,Me,CCl NOEt, a yellow aromatic oil -2 Chloral forms a com pound CCl₃ CHO(C₆H₃Me₂ C(NH) NOH) [112° crystallising in white scales, sol alcohol and ether but decomposed by water and dilute acids 3 ClCO₂Et acting on the amidoxim in chloroform forms C₆H₃Me₂ C(NH₂) NOCO₂Et [143°] which crystallises in white needles, v sol alcohol, ether, and chloroform, sl sol ligroin It is converted by heat into $C_6H_3Me_2C < N O > CO$ which crystallises in needles [182°], v sol alcohol and ether -4 Potassium cyanate acting on the hydrochloride of the amidoxim forms CaHaMe2 Č(NOH) NH CO NH2 [153°] which crystallises from dilute alcohol in white scales, and forms an unstable platinochloride — 5. Phenyl cyanate at 100° reacts forming C₈H₈Me₂C(NOH) NH CO NHPh [138°] which crystallises from alcohol in light yellow scales, sol acids, alcohol, ether, chloroform, benzene, and hot water −6 Phenyl thro-carbunde at 100° forms C₈H₈Me₂C(NOH) NH CS NHPh [150°], sol alcohol, ether, benzene, boiling water, and acids −7 Heating with Ap₂O forms the azoxim C₈H₈Me₂C⟨NO⟩ CCH₈ [89°] −8 Succinic anhydride fowns the azoxim C₈H₈Me₂C⟨NO⟩ CCH₂CH₂CO₂H which forms long white needles, [112°], v sol alcohol, ether, benzene, CHCl₈, and hot water, and yields crystalline salts

Acetyl derivative of the amidoxim C.H.Me. C(NOAc)NH. [189°] Small white needles, v sol alcohol and chloroform, al sol

ether (Oppenheimer, B 22, 2445)

Bensoyl derivative of the amidoxim C_sH₂Me₂C(NOB₂)NH₂ [158°] White crystals, v sol alcohol, ether, and chloroform, sl sol water and ligron Converted by heat into C_sH₂Me₂C(N) C_sH₃, which crystallises in faintly yellow scales, v sol alcohol, ether, and chloroform, volatile with steam (Oppenheimer, B 22, 2444)

Di-methyl benzoic acid C_eH₄Me₂.CO₂H_[5 2 1] p Xulene carboxulic acid [1327] (268° 1 V)

p Xylene carboxylic acid [132] (268° 1 V)
Formation —1 From bromo-p xylene by
treatment with ClCO₂Et and sodium amalgam,
the resulting ether being then saponified (Jacobsen, B 14, 2111) —2 By oxidation of methyl
xylyl ketone CH, CO C₆H,Me₂ [1 2 5] by dilute
HNO₂ or by kMnO₄ (Claus, B 18, 1858, 19,
3183) —3 From its amide

Salts - CaA'2 2aq crusts, m sol water -

BaA'2 4aq small needles

Amide C,H,Me, CONH, [186°] Formed by the action of Cl CO NH, (or of HNCO and HCl) on p xylene in presence of AlCl, (Gatter mann, A 244, 54, B 23, 1199) Colourless needles (from water), m sol hot water, v e sol alcohol

Dr-methyl-bensoic acid C₆H₃Me₂·CO₂H [3 2 1] o Xylenec carbovylic acid Hemimellithylic acid [144°] Formed by the oxidation of hem melithene C₆H₃Me₄, [3 2 1] by dilute nitric acid (Jacobsen, B 19, 2518) Prisms (from hot alcohol) or plates (from dilute alcohol) Volatile with steam, v sl sol hot water, insol cold water Yields o-xylene when distilled with lime CaA'₂ aq Long piisms, m sol cold water

Di-methyl benson said C,H,Me,.CO,H[4 3 1] o Xylene i carboxylic acid [165°] Obtained by boiling its amide for 2 days with caustic potash solution Formed also, together with the isomeric m-xylene i carboxylic acid [126°] (v supra), by oxidising \(\psi\$ cumene with dilute \) HNO₈ (Fittig a Laubinger, A 151, 275) Its ether is formed by the action of sodium-amalgam on a mixture of bromo-o xylene and ClCO₂Et (Jacobsen, B 17, 2874) Prisms (from alcohol), almost insol cold water, v sl sol boiling water, v e sol alcohol Gives o xylene when distilled with lime Gives C₄H₂Me(CO₂H)₂

[3 4 1] on oxidation with dilute nitric acid—CaA'₂ 3½aq Needles—BaA'₂ 4aq Needles, v. sol water

A mide C₆H₈Me₇CONH₂ [131°] Formed by the action of NH₂ COCl on o xylene in presence of ACl₂ (Gattermann, A 244, 52) Long shining needles (from water) The amide obtained from o xylene, gaseous cyanic acid, HCl, and AlCl, melts at 165° (Gattermann a Rossolymo, B 2°, 1199)

Diphenylamide C. H. Me. CONPh. [136°] From NPh. COCI, o xylene, and AlCI, (Lellmann a Bonhoffer, B 20, 2119) Small prisms v sol hot alcohol, sl sol ether and ligroin

Nttrite C.H.,Me., CN (232°) VD 461
Formed by fusing potassium o xylene sulphonate with KCy (Jacobsen, B 11, 23) Formed also by heating the corresponding xylenyl phosphate PO(OC,H.,Me.,), with KCy, the yield being 20 p c (Kreysler, B 18, 1711) Liquid, miscible with alcohol and ether

Di-methyl-benzoic acid C₆H, Me₂ CO₂H [5 3 1]

is described as MESITYLENIC ACID

Di-methyl-benzoic acid C₆H₃Me₂CO₂H?

Lauroxylic acid [155°] Produced by the action of dilute nitric acid on laurene C₁₁H₁₆
(Fittig, Köbrich, a Jilke, A 145, 151) Hard nodules (from alcohol) Nearly insol cold, al sol boiling, water, v sol alcohol Yields acetic acid on oxidation with chromic acid mixture — BaA'₂4aq Concentrically grouped needles, v sol water —CaA'₂4aq —AgA' White pp, may be crystallised from water

Tri-methyl-benzoic acid v \(\psi \) Cuminic acid Another tri methyl-benzoic acid, \(Hemimellithens \) carboxylic acid, is described as c-Cuminic acid.

Terra-methyl-benzoic acid C.HMe.CO.H. [5 4 3 2 1] [165°] (G), [150°] (C) (c 270°). Formed by oxidising penta methyl benzene, dissolved in benzene, with dilute nitric acid (dott-schalk, B 20, 3286). Formed also by oxidising tetra methyl-phenyl methyl ketone or tetra methyl-phenyl acetic acid with KMnO. (Claus, J pr [2] 38, 234). Needles (G), m sol hot water, v e sol alcohol, ether, benzene, CS2, and chloroform (C). Its alkaline salts are very soluble. The Ag salt is v sl sol water. The cupric salt forms light-green plates.—BaA'.2aq. Plates or nodules, v sol water and alcohol (G).—BaA'. 6aq (C).—CaA'. 3aq (C).—NaA'.3aq

Tetra-methyl-bensoic acid C.HMe, CO.H. [6 4 3 2 1] Formed by oxidising the corresponding C.HMe, CO.CH, with KMnO, (Claus a. Foecking, B 20, 3103) Yellow liquid, not solidified at 0°

Tetra-methyl-bensoic acid C_sHMe₄ CO₂H [6 5 3 2 1] [109°] (C a F), [112°] (G) Formed by oxidising the corresponding C_sHMe₄ CO CH₅ with KMnO₄ (Claus a Foecking, B 20, 3108). Formed also by boiling its amide for several days with alcoholic potash (G) Plates

Amade C. HMe, CONH. [178°] From durene, CICONH., and AlCl. (Gattermann, A 244, 55); Shining plates (from dilute alcohol)

244, 55): Shining plates (from dilute alcohol)
Tetra-methyl-bensoic acid C₆HMe₄ CO₂H
[179°] From durene COCl₂, and AlCl₃, the product being decomposed by water (Jacobsen, B
22, 1223) Also from O₅HMe₄ CO C₅H, and
KMnO₄ (Meyer a Ador, J 1879, 562) Must be identical with one of the three preceding acids,

probably with that of Gottschalk Large plates (from dilute alcohol), v sl sol cold water Volatile with steam May be distilled Cone HClAq at 210° yields durene and CO₂—CaA'₂ Short prisms, sl sol hot water —BaA'₂4aq Small plates (from hot water)

Methyl ether C. HMe, CO. Me [59°] (269° LV) Plates (Jacobsen, B 22, 1223) Saponified

by alcoholic potash at 210°

Nitrile C₅HMe₄CN [77°] Formed by distilling tetra methyl benzoic acid with PbCy₂ (Jacobsen, B 22, 1224) Needles, v e sol al cohol Split up by HCl at 215° into durene and CO₂ A crystalline nitrile C₅H(CH₃)₄CN [69°], (260°), probably identical with the last is formed by the isomeric change of the carbamine derived from duridine (q v) by distillation It is very stable towards HCl, by which it is not saponified to the acid, but at 250° it decomposes with formation of tetra methyl benzene (Hofmann, B 17, 1914)

Amide C_sHMe_s CONH₂ [173°] Formed by passing gaseous evanic acid and HCl into durene containing AlCl₃ at 100° (Gattermann a Rossolymo, B 23, 1199) It is probably the amide of the acid [179°], but has not been fully

examined

Penta-methyl-benzoic acid C₆Me₅ CO₂H [210 5°] Formed from penta methyl benzene, COCl₂, and AlCl₃ at 0°, after a fortnight the product is exposed to moist air and then treated with water (Jacobsen, B 22, 1220) Needles (from water) or prisms (from 70 pc alcohol), v sl sol cold, sl sol hot, water, v e sol hot alcohol Volatile with steam May be distilled With H₂SO₄ it yields C₆Me₅ and c durene (prehintene) HNO₃ forms di nitro c durene Fuming HClAq at 200° yields CO₂ and pentamethyl-benzene — CaA'₂ Prisms, m sol water—BaA'₂2aq Plates, sol hot water

water —BaA'₂2aq Plates, sol hot water Methyl ether MeA' [67 5°] (300° 1 V)

Plates, v sol alcohol

Amide C₆Me₅ CONH₂ [206°] From C₆HMe₅, chloro formamide, and AlCl. Plates, sl sol hot.

w sl sol cold, water

Nitrile C₄(CH₃), CN [170°] (J), [168°] (H) (292°) (H), (295°) (J) Formed from the carbamine C₆Me₅NC by intra-molecular trans formation by heating it a few degrees above its melting point (Hofmann, B 18, 1825) Large white needles, sol alcohol and ether, insol water It is remarkably stable, and could not be saponified by treatment with acids or alkalis. By heating with HI at 220°-230° it yields pentamethyl benzene, NH₂, and CO₂. Cone HClAq at 215° also yields C₆HMe₅.

METHYL-BENZOIC ALDEHYDE v Toluic

ALDEHYDE

Di-methyl-benzote aldehyde C₆H₄Me₂CHO [421] m Xylobenzaldehyde Xylyhc aldehyde, [-8°] (216°) Formed by oxidising di methyl-benzyl alcohol with K₂Cr₂O₂ and H₂SO₄ (Hinrichsen, B 21,3085, 22, 121) Separated by K₂CO₂ Colourless oil, volatile with steam HNO₃ oxidises it to di-methyl benzote and [126°].

Di-methyl-bensoic aldehyde C₆H₄Me₂ CHO [58 1] (221°) Formed from mesitylene by treatment in CS₂ with CrO₂Cl₂, followed by water (Etard, C. R 97, 909) The yield is almost the theoretical quantity Yields mesitylene and on

exidation.

Tri - methyl - bensoic aldehyde Phenyl hydrasıde Ma₂C₂H₂CH N₂HPh [129°] Formed by the action of tri methyl benzoic aldehyde on a solution of phenyl hydrazine in dilute HOAe (Rudolph, A 248, 100) Colourless needles, very sensitive to light, v sol ether, hot alcohol, and petroleum ether

DI - METHYL - BENZOÏN C₁₆H₁₆O₂ * e [4 1] C₄H₄Me CO CH(OH) C₆H₄Me [1 4] [89°] p Toluotn Prepared by boiling 10 pts of p toluic aldehyde (from p xylene) with 2 pts of KCy and 30 pts of 50 pc alcohol, and shaking the mass, after cooling, till the yellow product separates (Stierlin, B 22, 380, cf Grimaux a Lauth, Bl. 7, 233) Pale yellow prisms (from dilute alcohol), sl sol hot water, v sol alcohol, ether, and benzene Fuming H₂SO₄ gives a beautiful green colour

Acetyl derivative C_{1e}H_{1s}AcO₂ [100°] White crystals, v sol alcohol and ether Benzoyl derivative C_{1e}H_{1s}BzO₂ [119°]

White crystals, v sol alcohol and ether

METHYL BENZONITRILE v Nitrile of Toluic acid

Di-methyl-benzonitrile v Nitrile of Di-METHYL BENZOIC ACID

METHYL - BENZOPHENONE v PHENYL

TOLYL KETONE

Di-methyl-benzophenone v PHENYL XYLYL

KETONE AND DI TOLYL KETONE
TRI - METHYL - BENZOQUINONE CARB
OXYLIC ACID v \(\psi \)-Cumoquinone carboxylic

METHYL - BENZOYL - ACETIC ACID v. a Benzoyl propionic acid

"BaA'₂ faq prisms, si sol cold water —AgA'

TETRA - METHYL - BENZOYL - BENZOIC

ACID C₈HM₆, CO C₈H₄, CO₂H [2 1] Duroyl
bensoic acid [c 260°] Formed by heating phthalic

anhydride with durene in presence of AlCl,

(Friedel a Crafts, A Ch [6] 14, 454, C R 92,

833) Insol water, v sol alcohol, ether, and

benzene May be crystallised from HOAc The

Pb, Cu, and Ag salts are insol water —*KA'

minute needles, v sol cold water —*NaA', v

sl sol alcohol —*NH₄A' needles —BaA'₂ aq

groups of needles, v sl sol water —CaA'₂ aq

needles, v sl sol water

METHYL-BENZOYL-ETHYL-HYDROXYL-AMINE v Hydroxylamine derivatives

METHYL-DIBENZYL v PHENYL TOLYL-ETHANE

METHYL-BENZYL-ACETIC ACID v PHENYL-250 BUTYBIG ACID

DI-METHYL-BENZYL ALCOHOL C,H₁₂O t e [4 2 1]C_eH₄Me₂ CH₄OH Xylyl alcohol [22°] (232°) Formed by adding KNO₂ to a solution of dimethyl benzyl amine sulphate (Hinrichsen, B 21, 3085) Colourless liquid, with aromatic odour, volatile with steam Oxidised by chromia acid mixture to di-methyl-benzoic aldehyde

Acetyl derivative C.H.,OAc (230°-

Benzoyl derivative C.H., OBz (333°)

Yellow oil (Hinrichsen, B 22, 123)

Penta-methyl-benzyl alcohol C12H18O 2 e G.Me, CH, OH Mellityl alcohol [160 5°] tained by saponifying its acetyl derivative with alcoholic potash (Jacobsen, B 22, 1217)

metric prisms, insol water, v sol alcohol
Acetyl derivative CaMe, CH,OAc (310°) Obtained by the action of KOAc and HOAc on the chloride C.Me, CH, Cl, which is got by heating hexamethyl benzene with PCl, at 140° (Jacobsen) Plates or prisms (from alcohol), v sol ether, m sol alcohol at 0°, insol weter

o METHYL-BENZYL-AMINE

[2 1]C_sH,Me CH, NH₂ o-Tolyl methyl-amme Xylylamine (202°) Formed by heating methyl-benzyl phthalimide (derived from ω bromo-o xylene) with conc HClAq in sealed tubes at 200° (Strassmann, B 21, 577) Liquid, which absorbs moisture and CO from the air -B'₂H₂PtCl₈ yellow needles —B'HCl needles (from alcohol) -Picrate B'C₆H₃N₂O₇ long yellow needles, decomposing above 170°

Acetyl derivative C.H.Me CH2NHAC [69°] Formed by heating the hydrochloride with NaOAc and Ac.O Crystallises from alcohol

m Methyl-benzyl-amine

[3 1] $C_6H_4Me\ CH_2NH_2$ (202°) Formed by heating ω bromo m xylene with potassium phthalmide, and decomposing the product with cone HClAq at 190° (Bromme, B 21, 2700) Colour-Colourless liquid, miscible with alcohol and ether Absorbs CO₂ from the air—B'HCl needles B'.H₂PtCl_b [212°] Golden plates—Sulphate $[248^{\circ}] - B'_{2}H_{2}C_{2}O_{4}$ [172°] water — Picrate [156°] Plates, v sol

Acetyl derivative C.H.Me CH, NHAc

(235°-240°) Oıl

Benzoyl derivative C.H., Me CH., NHBz [69°] White plates (from alcohol), v sol chlo roform, HOAc, and benzene

p Methyl-benzyl-amine

[4 1]C₆H₄Me CH₂NH Formed by treating an alcoholic solution of the amide of this p toluic acid with zinc and HClAq (Paterno a Spica, B

8, 441)

m (?) Methyl-benzyl-amine C₆H₄Me CH₂NH (196) Formed, together with Xylylamine di methyl di benzyl amine and tri methyl tri benzyl amine by heating w chloro xylene with alcoholic NH, at 116° (Pieper, A 151, 129) Oil, smelling like herring brine. Is either the mcompound or a mixture Lighter than water Absorbs CO₂ from the air—B'HCl [185°] Needles, v sol water and alcohol -B'2H2PtCl6

Di m (?) methyl-di-benzyl-amıne $C_{1e}H_{19}N$ i e(C₆H₄Me CH₂)₂NH Formed as above (Pieper) Oil smelling like herring brine Lighter than water Decomposes above 210° -B'HCl [198°] Needles, sl sol cold water, v sol hot water and alcohol —B'HBr [196°]

Tri m (?) methyl-tri-bensyl-amine $C_{24}H_{27}N$ oil, si sol alcohol Cannot be distilled With bromine water it yields (C,H,Me CH,),NH and C,H,Me CHO —B'HCl [212°] (P), [204°] (Jannasch, A 142, 303) Needles, al sol cold alcohol, insol water and ether Heated in a

current of dry HCl it yields (C,H,Me CH2)2NH

and C₈H₄Me CH₂Cl —B'HNO₃ [122°] (J)

Di methyl-benzyl-amine C₈H₁N₁ e

[4 2 1]C₈H₄Me₂ CH₂NH₂. (219°) Xylyl-methyl
amine Xylobenzyl amine Formed by reducing with sodium the nitrile of the corresponding di methyl benzoic acid dissolved in alcohol (Hinrichsen, B 21, 3083, 22, 122) Liquid, sl sol water, v sol alcohol and ether Readily absorbs CO2 and moisture from the air Nitrous acid converts it into the corresponding alcohol
—B'HCl [210°] Needles or plates —B'_HLPtCl_,

[428°] —B'HHgCl_ [205°] —Nitrate [158°] —
Sulphate [254°] —Picrate [223°] —B'CdI_ — B',H2I2CdI2.

Benzoyl derivative C.H.2BzN Needles, v sl sol water, v e sol alcohol and

benzene

Di-methyl-benzyl amine BENZYL DI METHYL AMINE

METHYL-BENZYL ANILINE

C₆H₆NMe CH₂Ph (306°) (N), (above 360°) (S) From methyl anilne and benzyl chloride (Noelting, J 1883, 702, Stebbins, A C J 7, 42). Pale yellow oil

METHYL - BENZYL - BENZOIC p METHYL-BENZIL-BENZIL-C₁₅H₁₁O₂ te [4 1]C₅H₁Me CH₂C₆H₄CO₂H [134°] Formed from C₆H₁Me CO C₆H₄CO₂H by reducing with zinc dust and ammonia, filtering, diluting with water, adding HCl, dissolving the pp in NH₄Cl, and re ppg with acid (Gresly, A 234, 235) Long needles (from alcohol), v sol alcohol, HOAc, and benzene, almost insol water -BaA'₂ plates, v sol water

Di-methyl benzyl benzoic acid C16H16O2 2. [4 2 1] C, H, Me₂ CH. C, H, CO₂H[1 2] [188°] Ob tained by reducing C, H, Me₂ CO C, H, CO₂H with zinc dust and ammonia (Gresly, A 234, 237) Small needles (from alcohol) - BaA'asq Plates

(from dilute alcohol), sl sol water

METHYL-BENZYL BROMIDE v . Bromo XYLENE

DI METHYL-BENZYL CARBAMIC ETHER C₁₂H₁,NO₂ is [6 4 2 1]C₄H₂Me₅ NH CO₂Et

Mestlyl carbanuc ether [62°] From mesidine
and ClCO₂Et (Eisenberg, B 15, 1016) Long
needles (from water) Volatile with steam

METHYL-BENZYL-CARBINOL v PHENYL-

250 PROPYL ALCOHOL PENTA - METHYL - BENZYL CHLORIDE

C₆Me₅CH₂Cl [99°] (c 285°) Formed by heating C₆Me₆ (40 g) with PCl₃ (50 g) at 140° (Jacobsen, B 22, 1217) Plates (from alcohol ether), v e sol ether, sl sol alcohol TRI METHYL BENZYL CYANATE

[6 4 2 1]C₆H₂Me₂N CO (219°) From tri methylbenzyl carbamic ether and P₂O₅ (Eisenberg, B 15, 1017) Pungent liquid

METHYL-BENZYL GLYOXIM v. BENZYL-METHYL GLYOXIM

DI-w METHYL DI-BENZYLIDENE-ETHYL-ENE DIAMINE C18H20N21 e C2H4(N CMe C6H5)2 [c 104°] Formed by heating ethylene diamine (1 mol) with acetophenone (2 mols) to 120° White needles V sol alcohol and benzene, sl sol ether It is readily decomposed into its constituents, especially by acids (Mason, B 20,

METHYL BENZYL KETONE v BENZYL-METHYL-KETONE.

Methyl benzyl diketone $C_{10}H_{10}O_2$ i.e. (176°) SG $\frac{1}{2}$ 1 0721 CH, CO CO CH₂C₆H₅ (176°) S G 1 1 0721 This ketone is formed by distilling its monoxim CH, CO C(NOH) CH₂ C₆H₅ with FeCl, and dilute HCl (H Muller a Pechmann, B 22, 2133) Thick yellow oil, smelling like honey.

Dr-phenyl-drhydraside CH, C(N,HPh) C(N,HPh) CH2C,H, [173°]

Almost colourless flat silky needles

CH₃ CO C(NOH) CH₂C₆H₅ Mono oxim Isomtroso benzyl acetone [81°] Formed by the action of nitious acid on barium benzylacetoacetate (Ceresole, B 15, 1876, 3072, 16, Needles, insol ligroin May be sublimed 836) Dissolves in aqueous alkalis forming yellow solutions With NaOEt and benzyl chloride it gives CH₂ CO C(NOCH₂Ph) CH₂ C₆H₅, a thick yellow oil, volatile with steam

Di-oxim CH₃ C(NOH) C(NOH) CH₂ C₆H₅ Methylbenzylacetoximic acid [181°] by adding an alcoholic solution of hydroxylamine hydrochloride to an alcoholic solution of the mono-oxim (Schramm, B 16, 181, 218s) Small needles With Ac₂O it yields a di acetyl derivative CH₃ C(NOAc) C(NOAc) CH₂C₆H₅[80°]

METHYL-BENZYL MALONIC ACID BENZYL-METHYL-MALONIC ACID

o METHYL BENZYL-PHTHALAMIC ACID

 $C_{1e}H_{1b}NO_3$ 1 e [1 2] C_eH_4Me CH₂ NH CO C_eH_4 CO₂H[2 1]

o Xylyl phthalamic acid [156°] Formed by o methyl-benzyl phthalimide aqueous NaOH and ppg the solution with HCl (Strassmann, B 21, 576) Slender needles -AgA'

m-Methyl-benzyl-phthalamic acid

[1 3]C₆H₄Me CH₂ NH CO C₆H₄ CO₂H[2 1] [131°] Formed in like manner from m methyl benzylphthalimide (Bromme, B 21, 2700) Slender needles (from hot alcohol) -AgA' v sol boiling

o METHYL-BENZYL-PHTHALIMIDE

[1 2] C₆H,Me CH₂ N < CO > C₆H, [149°]

tained by heating ω bromo o-xylene with potassum phthalimide at 200°, the yield being 76 pc of the theoretical amount (Strassmann, B 21, 576) White hexagonal crystals (from alcohol), insol water With conc HClAq at 200° it forms methylbenzyl amine (202°) Aqueous NaOH converts it into o methyl benzyl phthalamic acid

m Methyl-benzyl-phthalimide

[18] C₆H₄Me CH₂ N CO C₆H₄

phthalimide [118°] Formed in like manner by heating ω bromo-m xylene with potassium phthalimide at 190° (Brömme, B 21, 2700) Slender hexagonal needles (from hot alcohol), v sol ether, chloroform, and alkalıs

METHYL-BENZYL-PIPERIDINE v BENZYL-METHYL-PIPERIDINE

METHYL BENZYL SULPHIDE CaH10S 26 CH, S CH, C, H, (195°-198°) Formed by heating benzyl chloride with Pb(SMe), at 100° (Obermeyer, B 20, 2926)

o Methyl-benzyl thiocarbimide C.H.NS 2 c. [21]C₆H₄Me CH₂ N CS o Xylyl throcarbinide (256°) Formed by boiling an ethereal solution of o-methylbenzyl-amine with CS, and HgCl.

(Strassmann, B 21, 578) Oil, smelling strongly like horse radish

D1-methyl-benzyl thiocarbimide $C_{10}H_{11}NS \ \imath \ \epsilon$ [4 2 1]C₆H₃Me₂.CH₂ N CS Xylobenzyl mustard oil Formed by heating the corresponding urea (C,H,Me, CH, NH),CO with syrupy phosphoric acid (Hinrichsen, B 22, 123)

METHYL-BENZYL-THIO-UREA

CH, NH CS NH CH, C,H, [74°] Formed by exposing an alcoholic solution of benzylamine mixed with methyl thiocarbimide for some days to the air (Dixon, C J 55, 619) White octa hedra, v sol hot benzene and hot alcohol, m sol ether Gives a black pp with ammoniacal AgNO₃, but the aqueous or alcoholic solution is not desulphurised by prolonged boiling with alkalıne lead tartrate

Methyl di-benzyl \(\psi \) thio-urea \(v \) DI BENZYL

METHYL-V-THIO UREA

o-Methyl-benzyl-thio-urea C,H, NS ic [2 1]C, H, Me CH, NH CS NH. o Xylyl thro urea [167°] Formed by evaporating a solution of potassium sulphocyanide and o methyl benzyl amine hydrochloride, and heating the residue to 140° (Strassmann, B 21, 578) White necdles (from water), m sol hot water Turns red in Alr

m Methyl-benzyl-thio-urea

[3 1]C,H,Me CH, NH CS NH, [112°] Prepared in the same way as the preceding body, using [3 1]C₅H₄Me CH₂NH₂ (Bromme, B 21, 2700)

Di m methyl-di-benzyl-thio-urea C, H, N,S e (C₆H₄Me CH₂ NH)₂CS [97°] Prepared by boil ing m methylbenzyl amine with alcoholic CS2

Needles, insol water, acids, and alkalis Tetra methyl-di-benzyl thio-urea $C_{19}H_{24}N_{\circ}S$ $(C_0H_3Me_2CH_2NH)_2CS$ **D**ixylobenzylsul phourea [177°] From (4, 2, 1) di methylbenzyl amine and alcoholic CS_2 (Hinrichsen, B22, 123) Glittering needles (from hot alcohol)

o METHYL-BENZYL-UREA CoH, 2N,O 1 c [2 1]C₆H₄Me CH₂ NH CO NH o-Xylyl urea [173°] Formed from o methylbenzyl amine sulphate and potassium cyanate (Strassmann, B 21, 578) Radiating moss like crystals (from alcohol), insol water

m Methyl-benzyl-urea

[3 1]C,H,Me CH, NH CO NH. [148°] Long needles from alcohol (Bromme, B 21, 2700)

D1-m-methyl-d1-benzyl-urea

 $(C_6H_4Me\ CH_2NH)_2CO$ [137°] Formed from m methylbenzyl-amine and COCl, in ethereal solution (B) Slender needles (from alcohol or ether)

Di-methyl-benzyl-urea C10H14N2O 2 e [4 2 1] C, H, Me, CH, NH CO NH, m Xylobenzyl-urea [184 5°] Formed by mixing concentrated solutions of (4, 2, 1) di methyl-benzyl amine hydrochloride and potassium cyanate (Hinrichsen, B 22, 122) Slender needles (from alcohol), m sol water from which it separates as a flocculent pp METHYL-BISMUTHINE v Bismuth methods

under Bismuth, organic derivatives

METHYL BORATES

Tri-methyl-borate Me, BO, (72°) (E a B), (65°) (S) SG 2 955 (E a B), 940 (S) VD 866 (E a B) Prepared by heating B,O, with methyl alcohol at 100° in sealed tubes, and distilling The distillate is freed from MeOH by shaking with conc H2SO4, and the upper layer is then rectified (Schiff, Bl [2] 5, 372, 6, 36) Formed also by the action of BCl, on dry methyl alcohol, the upper layer of the product being rectified (Ebelmen a Bouquet, A Ch [3] 17, 59, A 60, 251) Colourless mobile liquid, sol alcohol and ether Burns with a green flame (greener than that of Et.BO.) Decomposed by water into boric acid and MeOH

Methyl metaborate MeBO A thick liquid. formed by heating Me, BO, with BO, When heated, it begins to decompose a 160° giving off Me.BO, and at 250° there remains a mass of the composition MeB,O, which becomes vitreous

on cooling

An acid methyl rorate Me B.O. was described by Ebelmen (A Ch [3] 16, 1.7) as obtained by treating BO, with dry MeOli, and as being a vitreous mass, readily decomposed by water into boric acid and MeOH It was probably a mixture of Me, BO, and MeBO,

METHYL-BORNYL UREA BORNYL-

METHYI UREA

TRI-METHYL-BRAZILIN C16H11Me3O5 3aq Formed in the preparation of tetra methyl brazilin (v infra) Crystalline, sol dilute alco hol Its solution in aqueous NaOH is colourless

and gives a brown pp with FeCl,

Acetyl derivative C₁₆H₁₀AcMe₃O₅ [97°]
Tetra-methyl-brazilin C₁₇H₁₀Me₄O₅ [139°] [139°] Formed by the action of NaOEt and MeI on brazilin (Schall a Dralle, B 20, 3365, 21, 3009) Snow white crystals Bromine in HOAc forms C16H9BrMe4O, [181°] and crystalline di bromo tetra methyl brazilin dibromide C16H8Br Me4O3

METHYL-BROMACETOL aa Di bromo-I ROPANE

METHYL BROMIDE CH.Br Bromo methane Mol w 95 (45°) SG ${}_{8}^{8}$ 17331, ${}_{2\overline{2}}^{2}$ 17235 (Perkin), ⁰/₂ 1 732 (Merrill) V D (H=1) 95 M M 4 644 at 15° (Perkin, C J 45, 454) H F p 14,700 H F v 14,210 (Phomsen) S V 55 7 (Lossen, A 254, 68)

Preparation - Methyl alcohol (800 grms) and amorphous phosphorus (133 grms) are put into a retort Bromine (800 grms) is slowly After some hours the retort is heated and the product condensed in a receiver surrounded by a freezing mixture. It is washed with dilute potash, dried over calcic chloride and distilled (Merrill, J pr 126, 296, cf Pierre, J Ph [3] 13, 156, Bunsen, A 46, 44)

Properties - Colourless, mobile liquid, with burning taste and pleasant smell resembling chloroform Burns with greenish brown smoky flame Miscible with alcohol, ether, chloroform, and CS₂ Poured into cold water a white ice like mass is formed It is approximately CH, Br, 20aq At 5° it begins to split up with evolution of methyl bromide gas

METHYL-BROMO-ACETOACETIC ETHER v

Bromo aceto-acetic acid

METHYL-BROMO-ACETOL v DI BROMO PRO-

METHYL a-BROMQ-ALLYL OXIDE C,H,BrO e CH, O CH, CBr CH. (116°) SG 10 135 Formed by the action of NaOH CH, O CH, CHBr CH, Br (Henry, B 5, 455)

METHYL BROMO - ALLYL SULPHIDE C.H.BrS to CH. S CH. CH CHBr Formed by heating Pb(SMe), with s-tri-bromo propane in

ethereal solution at 150° (Obermeyer, B 20, 2925) Decomposes at 120°-130° Combines Combines with Br (1 mol)

METHYL-BROMO-AMINE v METHYLAMINE METHYL-DI-BROMO-ANTHRACENE v 1/1. BROMO METHYL ANTHRACENE

METHYL-DI-BROMO ATROLACTIC ACID v. DI BROMO OXY-TOLYL PROPIONIC ACID

METHYL BROMO - BUTYL KETONE ACETYL BUTYL BROMIDE

TRI METHYL - BROMO - ETHYL AMMO-NIUM BROMIDE v TRIMETHYLAMINE bromo. ethylo bromide

METHYL-BROMO ISATIN v Methyl derivative of Bromo Isatin, p 71

METHYL BROMO ISATOID v Bromo methylisatoid, p 71

METHYL BROMOPROPYL KETONE

CH₂ CO CH₂ CH₂ CH₁ Br Acetyl propyl bromide. (118°) at 90 mm (P), (106°) at 60 mm (L) Formed by treating acetyl propyl alcohol (q v) with a saturated aqueous solution of HBr (Colman a Perkin, jun, C = J = 55, 357, Lipp, B = 22, 1196) Colourless mobile liquid with penetrating Turns brown in light SI sol cold odour water, quickly decomposed by hot water, dissolving as acetyl propyl alcohol Forms a crystalline compound with NaHSO, NaOEt and KOH act on it, forming a light ethereal oil C.H.O (113°), probably methylene furfurane tetrahydride

METHYL BROMO-STYRENE v BROMO TOLYL-

METHYL BRUCINE v Methylo- compounds of Brucine, vol 1 p 637

BUTENYL TRICARBOXYLIC METHYL **ACID** v Pentane tricarboxylic acid

METHYL BUTENYL KETONE vACETONE

METHYL ISOBUTYL ACETAL v ALDEHYDE METHYL-BUTYL-ACETIC ACID v Heptoic

ACID Methyl-di-butyl acetic acid v Hendecore

METHYL-BUTYL-ACETYLENE v HEPTIN-

METHYL-ISOBUTYL ANILINE C,,H,,N . e $C_{e}H_{s}NMe CH_{2}Pr (235^{\circ})$ (Noelting, J 1883, 702). METHYL - ISOBUTYL - BENZENE v Iso-

BUTYL TOLUENE METHYL - BUTYL - CARBINOL v HEXYL

ALCOHOL Di methyl butyl-carbinol v HEPTYL ALCOHOL.

METHYL ISOBUTYL CARBONATE C.H. O. te CH,O CO OC,H, (143 6° cor) 8 G 17 95 (Rose, A 205, 230)

DI - METHYL - BUTYLENE - DIKETONE C.H.O. re CH. CO CH. CH. CH. CH. CH. CO CH. Dr-acetyl butane [44°] Obtained by heating its dicarboxylic ether with NaOMe in MeOH (Marshall a Perkin, jun, C J 57, 241) Crystalline mass, sl sol water, v sol other menstrua Combines with NaHSO, Reacts with phenylhydrazine and with hydroxylamine Boiling alcoholic potash condenses it forming methylpenta methenylyl trihydride methyl ketone $CH_{\bullet}C < C(COCH_{\bullet}) > CH_{\bullet}$

DI - METHYL - BUTYLENE - DIKETONE CARBOXYLIC ETHER C11H18O, 10 CH2 CO CH2 CH2 CH4 CH(CO2Et) CO CH2.

di-acetyl n valeric ether (195°-200°) at 100 mm. Obtained by distilling the corresponding di-carboxylic ether (di-acetyl adipic ether) with potash, neutralising the residue with H2SO4, extracting with ether, washing the ether with water, drying and evaporating (Perkin, jun, C J 57, 229) Colourless oil, v sol ether and alcohol, sl sol water Its alcoholic solution is coloured violet by FeCl, On hydrolysis it yields acetyl-valeric acid and acetic acid

D1-methyl-butylene-diketone dicarboxylic ether C₁,H₂O₅ te CH₃ CO CH(CO₂Et) CH₄,CH₂CH(CO₂Et) CO CH₃ Ethylene diaceto acetic ether Di acetyl adipic ether Formed by the action of sodium (40 g) on aceto acetic ether (260 g) and ethylene bromide (190 g), dissolved in alcohol (Perkin, jun, C J 57, 215) It may be purified by conversion into the yellow flocculent di sodium compound (Ac CNa(CO₂Et) CH₂)₂, decomposing this with very dilute HCl, and extracting with ether Thick oil, miscible with alcohol and ether, sl sol dilute aqueous KOH FeCl, colours its alcoholic solution intense violet red Combines with great difficulty with NaHSO₃ Decomposed by heat into di-methyl butylene diketone carboxylic ether, and the two ethers

C(CH₃) C CO CH₃ and CO₂Et CH CH, CH₂ C(CH₃) C CO₂Et Alcoholic ammonia

CO.Et CH CH, CH,

converts the dicarboxylic ether into the di imide (CH₃ C(NH) CH(CO₂Et) CH₂)₂ [174°] which is reconverted by warming with dilute HCl into the

original ketonic ether

Phenyl hydrazide (CH₃ C(N₂HPh) CH(CO₂Et) CH₂)₂ Formed by heating di methyl butylene diketone carboxylic ether with phenyl hydrazine on the water bath (Perkin, jun, a Obremsky, B 19, 2049, Perkin, jun, C J 57, 221) Plates or needles (from MeOH), v sol cone HClAq, insol alkalis, v sl sol ether At 200° it gives off EtOH (2 mols), forming di oxy di phenyl dimethyl ethylene - di - pyrazole tetrahydride CO CH CH, CH, CH CO

CMe CMe `N ĊMe METHYL-ISOBUTYL-GLYOXALINE thylo rodide CoH1, N2I re N2C2H2MeC4H9MeI Formed by treating isobutyl glyoxaline (glyoxal-isoamyline) with MeI in MeOH (Radzis zewsky a Szul, B 17, 1294) Trimetric prisms (from alcohol)

\NPh

METHYL-n-BUTYL KETONE CH, CO C.H. (127°) SG 2.830 Formed by the oxidation of sec hexyl alcohol (Erlenmeyer a Wanklyn, A 135,

144, Schorlemmer, A 161, 263) Combines with NaHSO, Gives on oxidation acetic, nbutyric, and valeric acids (Wagner, B 18, 2267)

Methyl isobutyl ketone CH, CO CH, Pr (115°) S G § 8195, 19 8034 (Wagnes, J R 16, 703) A product of the distillation of potassium isovalerate with NaOAc (Williamson, 4 Formed by the action on valeryl chloride of ZnMe, followed by water Formed also by boiling isopropyl-aceto acetic ether with baryta water (Frankland a Duppa, A 145, 82)

Combines with NaHSO. Yields on oxidation acetic, isobutyric, and isovaleric acids

Methyl sec-butyl ketone CH, CO CHMeEt S G 14 5 8181 Formed by boiling (118° 1 ♥) methyl ethyl acetoacetic ether with dilute KOH or baryta water (Wishcenus, A 219, 307, Wagner, J R 16, 711) Oil, smelling of peppermint Oxidised by chromic acid mixture to methyl ethyl ketone and HOAc Sodium reduces it to the corresponding nexyl alcohol and methyl sec butyl pinacone [249°]

Methyl tert-butyl ketone CH, CO CMe, (105 3°) (Schiff, B 19, 562) SG. Pinacoline

2 8265, 1ª 800

Formation —1 By distilling pinacone with dilute sulphuric acid (Fittig, A 114, 56) —2 By the action of CMe, COCl on ZnMe, followed by water (Butlerow, A 174, 125) —3 By the dry distillation of calcium isobutyrate (Barbaglia a Gucci, B 13, 1572)

Properties -Liquid, smelling of peppermint, nearly insol water Sodium amalgam forms the corresponding hexyl alcohol with NaHSO₃ Chlorine forms pungent C₆H₁₀Cl O

crystallising in needles [51°], (178°) Oxim CH, C(NOH) CMe, [75°] Slender needles, very volatile with steam (Janny, B 15, 2780) May be sublimed Sl sol cold, v sol hot, water Has a camphor like smell and taste Not decomposed by acids

Methyl isobutyl diketone C,H12O CH, CO CO CH, CH(CH,) Acetyl isovalcryl Diketoheptane (138°) S G 22 908 Formed by distilling its mono oxim with dilute H SO (Otte a Pechmann, B 22, 2122) Yellow oil with irritating smell, becoming fruity when di Sl sol water

Mono oxim CH, CO C(NOH) CH2Pr Ni troso isobutyl acetone [42°] Formed by adding NaNO, (10g) to a solution of isobutyl aceto acetic ether (27g) in water (300 cc) and KOH (8g), and extracting with ether (Treadwell a Westenberger, B 15, 2786) White plates, v sol alcohol and ether, sl sol cold water, dis solves in alkalis

CH₃ C(NOH) C(NOH) CH Pr DioximSmall white shining plates (from [c 172°] dilute alcohol) (O a P)

Oxim phenylhydrazide C₁₃H₁₈N₃O i e CH₃C(N₂HPh) C(NOH) CH₂Pr [151°] Almost colourless needles

Phenylhydrazide C₁₃H₁₈N₂O [98°] Almost colourless needles

Diphenylhydrazide CH₃ C(N₂HPh) C(N₂HPh) CH₃Pr [116 5°] Almost colourless needles

METHYL n BUTYL KETONE CARBOXYLIC ACID C,H,1O, i e
CH, CO CH, CH, CH, CH, CO, H

valeric acid [42°] A product of the hydro

lysis of di methyl butylene diketone carboxylic ether by a solution of KOH in methyl alcohol (Perkin, jun, C J 57, 231) Colourless crystals, v sol water, alcohol, and ether Its ammo nium saltis very soluble —AgA' leafy masses The cupric salt forms (from hot water) minute spherules

METHYL-ISOBUTYL-KETONE SULPHONIC ACID CH₂ CO C₁H₂(SO₂H) The sodium salt of this acid is slowly formed by the action of a saturated solution of NaHSO, on mesityl oxide It is easily soluble in water and alcohol, melts at 95°, is not attacked by Na₂CO₂, but by NaOH it gives mesityl oxide (Pinner, B 15, 592)

METHYL BUTYL KETOXIM v. Oxim of

METHYL BUTYL KETONE

METHYL n BUTYL OXIDE C3H12O 16 CH, OC,H, (703°) SG \$ 7635 SV 1 CE (0°-10°) 00125 (Dobreiner, A 243, 3) 127 2

Methyl isobutyl oxide CH, O CH₂Pr One of the products of the action of NaOCH₂Pr on methylene iodide oi iodoform (Gorboff, J pr Oil Conc HIAq yields MeI [2] 41, 238, 254) and isobutyl iodide

METHYL-ISOBUTYL-PHENOL C11H16O 1 e $C_6H_3(CH_3)(C_4H_9) OH[1 3 6]$ (236°) Isobutyl o cresol Formed by the action of nitrous acid on methyl isobutyl phenyl amine (Effront, B 17, 2324) Oil V sol alcohol and ether, nearly insol water

Isomeride v Methyl ether of Isobutyl-PHENOL

METHYL-ISOBUTYL PHENYL AMINE

 $C_0H_3(CH_3)(C_4H_9)NH_2[1\ 3\ 6]$ Isobutyl tolyl (243°)amine or toluisobutylamine Formed by heating o toluidine hydrochloride with iso butyl alcohol at 200°-300° (Effront, B 17, 2317) Colourless liquid Volatile with steam Miscible with alcohol and ether, nearly insol water

Salts -B'HCl Long thin needles, sl sol cold water, v sol hot water -B'HBr long soluble needles -B'.H SO, needles, sl sol cold water - B' H₂C₂O₄ silvery needles, insol ether

Formyl derivative C11H15 NH(COH) [106°] Colourless tables, v sol alcohol and ether, nearly insol cold water

Actual derivative C,H, NHAc [162°] Colourless plates, sparingly sol hot water, easily

Benzoyl derivative C,H, NHBz [168°] Small white needles, insol cold water, v sl sol hot

METHYL-ISOBUTYL PHENYL-AMINE

 $C_{1}H_{2}(CH_{2})(C_{1}H_{2})NH_{1}[1\ 5\ 6]$ (244°) by heating o toluidine with isobutyl alcohol and ZnCl. at 270°-280° (Effront, B 17, 2339) Colourless liquid Volatile with steam

Salts -B'HCl Plates -B'2H2SO4 plates

-B'.H C.O. easily sol ether Formyl derivative $\mathbf{C}_{11}\mathbf{H}_{10}$ NH(CHO) White plates, v sol alcohol and ether, nearly insol water

Acetyl derivative CnH15 NHAc [141°] Long silky needles

Benzoyl derivative C11H15 NHBz [142°] Silvery plates

MÉTHYL - ISOBUTYL - PHENYL - DI -**METHYL-AMINE** $C_6H_3(CH_3)(C_4H_9)NMe_2[1 \ 3 \ 6]$ Dimethyl toluisobutylamine (250°) Colourless Formed by methylation of methyl iso butyl phenyl amine -B'2H2Cl2PtCl4 (Effront, B 17, 2339)

DI METHYL-DI-BUTYL-DI PHENYL-THIO-UREA v DI BUTYL DI-TOLYL THIOUREA

METHYL BUTYL PINACONE DI-OXY-DODECANE

DI METHYL DI ISOBUTYL-PYRAZINE

 $N \leqslant_{\mathbf{C}(C_4\mathbf{H}_9)}^{\mathbf{CMe}} \stackrel{\mathbf{C}(C_4\mathbf{H}_9)}{\mathbf{CMe}} N D_i$ isobutyl-C,4H24N2 2.6 (243°)Formed by reducing the oxim of methyl isobutyl diketone Me CO C(NOH) C.H.

with tin and HCl (Lang, B 18, 1364, Oeconomides, B 19, 2526, Wolff, B 20, 433)

oil -B'H.PtCl₆ orange needles
DI METHYL ISOBUTYL PYRIDINE C11H1,N $N \leqslant_{CMe\ CH}^{CMe\ CH} > C C_4H_4$ Isobutyl lutidine. (210°-213°) S G 12 8961 Formed by distilling its carboxylic acid with lime (Engelmann, A 231, 65) Oil, smelling of violets Tastes bitter More soluble in cold water than in hot water -B₂H,PtCl₆. [209°] Yellow crystalline pp -B',H,Cr,O, Yellow plates, v sol boiling water -Picrate [115°] Yellow needles

Hexahydride C11H22N 1e

NH CHMe CH₂ CH C,H, s Isobutyl lupe-Di methyl isobutyl piperidine at 720 mm Formed by reducing di methyl isobutyl pyridine in alcoholic solution with sodium (Jaeckle, A 246, 47) Oil With NaNO, and HCl it yields a nitroso compound — B'HCl [184°] Prisms, v sol water and alcohol—B'HBr Prisms The platinochloride and chromate could not be crystallised

DI METHYL-ISOBUTYL PYRIDINE DI-CARBOXYLIC ACID C12H17NO4 1 e

N≪CMe C(CO,H)>C C,H, [273°] Formed by boiling its diethyl ether with alcoholic, and afterwards with aqueous, potash (Engelmann, A 231 57) Long monoclinic prisms (containing Decomposed by fusion M sol cold, v sol hot, alcohol -CaA"3aq Small four-sided pyramids, v sol water -BaA"5aq -H2A"HCL M sol cold water

HEtA" [135°] Mono ethyl ether Formed by boiling the di ethyl ether with alco holic potash Long prisms, v sol water and alcohol -Ba(EtA") 5aq -HEtA"HCl2aq thick prisms

Et,A" Diethylether (312°-318°) Formed by passing nitrous acid gas into an alcoholic solution of its dihydride Thick oil -It A' HCl long needles, decomposed by water into HCl and Et₂A' -(Et₂A")₂H₂PtCl₆ [208°]

Cubes Dihydride of the diethyl ether

NH Cyle C(CO H) CH C,H, [100°] Formed by warming acetoacetic ether with isovaleria aldehyde ammonia in alcohol (E) Long prisms. v sol alcohol, ether, and benzene

METHYL ISOBUTYL SULPHATE C,H12SO, ie (CH3)(C4H9)SO4 appears to be formed by the action of methyl alcohol on C,H,O SO,Cl, the product of the action of isobutyl alcohol on SO.Cl., (Behrend, J pr [2] 15, 34) Decomposed by water into HOMe and C₄H₉O SO₄OH

DI METHYL ISOBUTYRYL-ACETIC ETHER

v Di isopropyl ketone carboxylic ether METHYL CAFFEIC ACID v Caffeic acid METHYL CAFFURIC ACID v CAFFEINE

METHYL CARBAMATE NH₂ CO₂Me Methyl urethane [52°] (G), [56°] (F a K) (177°). Formed from NH, COCl and excess of methylalcohol (Gattermann, A 244, 39) Formed also from C.H.(N(NO.) CO.Me), by the action of NH₈ (Franchimont a Klobbie, R T C 7, 343)

METHYL CARBAMIC ACID *NHMe CO2H The methylammonium salt NHMe CO,NH,Me appears to be formed by passing CO, into dry methylamine (Wurtz, A Ch

[8] 30, 450, 461)

Methyl ether NHMe CO.Me (158°) SG 15 1065 Formed by treating methyl chloro formate Cl CO, Me with an aqueous solution of methylamine (Franchimont a Klobbie, R T C Colourless liquid, with characteristic With pure HNO₃ it yields a character odour' istic nitro- derivative

Ethylether NHMe CO2Et (170°) Formed from methylamine and chloro formic ether (Schreiner, J pr [2] 21, 124) Oil, with pleasant When boiled with potash or baryta it yields alcohol, methylamine, and K2CO3

NHMe COCl From COCl₂ and methylamine hydrochloride (Gattermann a Schmidt, B 20, 118)

posed on boiling

Di methyl-carbamic acıd *NMe, CO,H

Methyl ether NMe₂CO₂Me (131°) SG 15 1012 Formed by treating Cl CO OMe with an aqueous (33 p c) solution of dimethylamine (Franchimont a Klobbie, R T C 8, 299) Colourless liquid, smelling like menthol Pure HNO, forms NMe(NO.) CO.Me

Ethyl ether NMe, CO,Et (140°) (Schreiner, J pr [2] 21, 125), (147°) (Franchimont a Mobbie, R T C 3, 223) SG 11 978 From With ammonia Cl CO Et and dimethylamine

obloride NMe₂ CO NH₂ Chloride NMe₂ COCl (1 (165°) From dimethylamine and a solution of COCl₂ in benzene (Michler a Escherich, B 12, 1162) with peculiar odour, v sol ether and CS₂ Decomposed slowly by water into HCl, dimethylamine, and CO,

METHYL CARBAMINE C2H3N te CH3N C Methyl isocyanide Methyl cyanide Methyl mine Isoacetomirile Mol w 41 (596°) V D 144 (calc 142) S G S 10 at 15° Formed by the action of carbylamine ₹ 75**6** MeI (1 mol) on silver eyanide (2 mols) the product being decomposed by KOH and dried over CaCl₂ (Gautier, C R 63, 924, 65, 468, 862, 66, 1214, A 152, 222, A Ch [4] 17, 203) Formed also by the action of MeI on mercuric fulminate (Calmels, J pr [2] 30, 319, C R

Properties -Liquid with powerful odour,

producing nausea

Reactions -1 Aqueous acids decompose it into methylamine and formic acid -2 HOAc forms CH₈NH CHO and Ac₂O —3 Oxidised by HgO at 50° to methyl cyanate CH,N CO and a compound Me₃N₃C₃O₃(NH₂ CHO) [175°] in ethereal solution appears also to form diin ethereal solution appears also to form differmamide NH(CHO)₂ or, rather, a compound Me₂N₃C₃c₃(NH(CHO)₂) [163°] (Gautier, C R 67, 804)—4 With AgCy it forms a compound MeNCAgCy [80°-90°] (Meyer, J 1856, 528) Salt—(MeNO)₂3HCl. Formed by passing HCl into an ethereal solution of methyl carbanna Creatallyna Becomposed by water. Crystalline Decomposed by water, partially reproducing methyl carbamine — 5 MeI acts in a complicated manner (Lubavine, Bl. [2] 45, 246, Gautier, A Ch [4] 17, 148)
Tri-methyl-carbsmine. A name used by

Rudneff (Bl [2] 33, 297) to denote tert-Buttle-

METHYL-SEMI-CARBAZIDE C,H,N,O ... NH. CO NH NH. Me [113°]. Formed from

methyl-hydrazine acid sulphate KHO and KCNO (Bruining, A 253, 10) Prismatic tables, v sol water and EtOH, m sol ether

METHYL-CARBAZOLE C15H11N 4.6

>NMe [87°] Formed by heating potas C'H' sium carbazole with MeI at 180° (Graebe, A 202, 23) Micaceous leaflets or needles, insol water, sol ether Conc H SO, containing a little HNO, gives a green colour—Picrate C₁₅H₁₁NC₆H₂(NO₂)₃OH [141] Dark redneedles METHYL CARBIMIDO ALLYL-THIO UREA

 $SC <_{\rm NH}^{\rm NC_3H_5} > C \ {\rm NMe} \ \ {\rm or} \ \ C_3H_5 \ {\rm NH} \ {\rm CS} \ {\rm N} \ C \ {\rm NMe}$ Allyl-thro-carbamine-methyl cyamide Formed by the action of methyl iodide upon sodium carbimido allyl thio urea Crystalline sol water and alcohol Indifferent body (Wunderlich, B 19, 448)

METHYL-CARBIMIDO-ETHYL-THIO-URBA

SC<NEt>C NMe or EtNH CS N C NMe

Ethyl-thro-carbamine-methyl cyamide Formed by the action of methyl iodide upon sodium carbimido ethyl-thio-urea (Wunderlich, B 19, 448)

TRI-METHYL CARBINOL v Tert Butyl ALCOHOL

METHYL CARBONATES

Hydrogen methyl carbonate *MeHCO3 The Ba salt, Ba(MeCO₃), appears to be the white pp formed when CO₂ is passed into a solution of BaO in anhydrous methyl alcohol (Dumas a Péligot, A Ch [2] 74, 6) It is insol alcohol, but dissolves in water, the solution soon depo siting BaCO.

Di-methyl carbonate C,H₃O₃ v e (CH₃).CO₃ [0.5°] (Röse, A 205, 231) (91°) S G = 1 069 HFp 138,890 HFv 136,360 (Thomsen, Th)
Formed by boiling methyl chloroformate ClCO₂Me with lead oxide (Councler, B 13, 1697) Formed also from ClCO₂Me and NaOMe (Schreiner, J pr [2] 22, 354) Oil, insol water, sol alcohol and ether Converted by dry chlorine into hexa-chloro di methyl carbonate $(q \ v)$

METHYL-CARBOPYRIDIC ACID v METHYL-PYRIDINE CARBOXYLIC ACID

METHYL-CARBOSTYRIL v Methyl ether of CARBOSTYRIL and OXY METHYL QUINOLINE

METHYL CETYL KETONE C18H18O 16 C₁₆H₃₈ CO CH₃ [52°] (252° at 100 mm) Formed by distilling a mixture of barium margarate and barium acetate (Krafft, B 15, 1707). Yields palmitic and acetic acids on oxidation

METHYL-CHELIDAMIC ACID v CHELIDONIC

METHYL-CHLORACETOL 12. DI CHLORO-PROPANE

CHLORIDE METHYL CH,Cl Chloro. methane Mol w 50.5 (-28 7°) (Regnault) V D 178 (calc 175) S G 22 9915, 2 9523 (Vincent a Delachanal, A Oh [5] 16, 429) S 5 03 at 7°, 8 46 at 20° (Baeyer, A 107, 181) S, (alcohol) 35 S (HOAc) 40 HFp 22,550 HF v 21,970 (Thomsen) S V 50.8 (Lossen, A 107, 181) A 254, 68) Latent heat of evaporation 96,900

at 0° (Chappus, A Ch [6] 15, 507)

Formation —1 By heating a mixture of NaCl (2 pts), wood spirit (1 pt) and H₂SO₄ (8 pts) and collecting the gas over water (Dumas a. Péligot, A. Ch. 61, 193, A. 15, 17) — 2 By exposing a mixture of equal volumes of methane and chlorine to daylight (Berthelot,

A Ch [3] 52, 97)

Preparation—1 HCl is passed into MeOH (2 pts) containing ZnCl, (1 pt) The gas is passed through KOH and H.SO, (Groves, C J 27,641, A 174,378)—2 By heating trimethylamine hydrochloride at 260°, the reaction being perhaps 3NMe₃HCl = 2NMe₃ + NH₂ + 3MeCl (Vincent, J Ph [4] 30, 132)

Properties — Colouriess gas, with ethereal odour Burns with a bright flame, edged with

green

Reactions -1 When passed through a redhot tube it deposits charcoal and yields HCl, methane, ethylene, CO, and naphthelene (Perrot, A 101, 375)—2 When passed over heated potash-lime it yields potassium formate, KCl, and hydrogen -3 Not attacked by chlorine in diffused daylight, but when the mixture is exposed to direct sunlight, substitution occurs, the products being methylene chloride, chloroform, and CCl. The chlorination may also be effected by passing a mixture of chlorine and methylchloride over animal charcoal at $250^{\circ}-350^{\circ}$ (Damoiseau, C R 92, 42) -4 When equal volumes of methyl chloride and of an amine are submitted to a piessure of 25 atmospheres for 48 hours the following reactions occur—(a) Ammonia forms NMeH,Cl, NMe,HCl, and 2NH, Cl -(b) Methylamine forms 2NMeH, Cl and NMe Cl —(c) Dimethylamine reacts with forma tion of NMe H,Cl and NMe,Cl -(d) Trimethylamine forms NMe,Cl (Vincent a Chappuis, Bl [2] 45, 496)

Hydrate MeCl 9aq Formed by cooling below 0° water into which MeCl is passed Its vapourtension has been studied by De Forcrand a Vil-

lard C R 106, 1357, 1404)

METHYL-CHLORO-ALLYL CARBINOL v Chloro pentenyl alcohol

DI-METHYL-CHLORO-ANILINE v CHLORO DI METHYL ANILINE

TRI-METHYL CHLORO-AURO-PHOSPHITE Me,PAuClO, [101°] Formed by the action of pure methyl shochol on aurous chloride and phosphorus (Lindet, C. R. 103, 1014) Slender colourless needles, insol water, sol MeOH

METHYL CHLORO-BUTYL CARBINOL v

CHLORO HEXYL ALCOHOL

METHYL - CHLORO - CARBOSTYRIL

CHLORO OXY METHYL QUINOLINE

METHYL CHLORU-ETHYL OXIDE C₃H ClO te CH₃ CHCl OMe (72°-75°) S G ¹⁷ 990 Formed from aldehyde (1 vol), methyl alcohol (1; vols), and dry HCl at 0° (Geuther, A 225, 270)

METHYL TETRA-CHLORO-ETHYL OXIDE C,H,Cl,O :s CCl, CHCl O CH, (178°) S G 2 184 Formed by the action of PCl, on chloral methylate (Magnanini, G 16, 330) Colourless liquid

METHYL CHLORO-FORMAMIDE v CHLORO FORMIC ACID

METHYL CHLORO - PROPYL KETONE C₃H₁ClO 1.5 CH₂CO CHClEt (130°) Formed by heating CH₃CO CClEt CO₂Et with dilute HCl at 180° (Conrad, A 186, 241)

Methyl tri-chloro-propyl ketone C₃H₂Cl₃O t.s CH₄CO C₂H₄Cl₂ (193°) Formed by oxidising

C₂H₄Cl₄ CHMe OH with chromic acid mixture (Garzarolli Thurnlackh, A 223, 152) oil Does not combine with NaHSO₂ Yields CO₂, acetic acid, and HCl on oxidation

DI METHYL - CHLORO - QUINALDINE .

CHLORO TRI METHYL QUINOLINE

METHYL-TRI CHLORO-QUINOLINE v TRI-CHLORO METHYL-QUINOLINE

METHYL DI-CHLORO-VINYL OXIDE C₃H₄Cl₂O te CCl, CH O CH₂ (110°) S G 2 12934, ¹⁰² 11574 Prepared by heating trichloro ethylene with KOMe, being ppd on addition of water (Denaro, G 14, 117) Colourless oil, with an odour resembling that of acetal Decomposed on exposure to air, with evolution of HCl When heated with dilute H₂SO₄ it yields di chloro acetic orthaldehyde

Methyl tri chloro-vinyl oxide CCl₂ CCl O CH, Readily absorbs dry oxygen, forming the compound COCl CCl(OMe), which, by the action of water, gives oxalic acid (Henry, B 12.1838)

METHYL CHRYSOIDINE v Benzene-Azo methyl phenylene dramme

METHYL-CINCHENIC ACID v CINCHENE
METHYL-CINCHONAMINE v CINCHONA

DI-METHYL-CINCHONIC ACID v Dr METHYL QUINOLINE CARBOXYLIC ACID

METHYL-CINCHONIDINE v CINCHONIDINE
METHYL-CINCHONINE v CINCHONINE
METHYL CINNAMIC ACIDS v PHENYL-

METHACRYLIC ACID and TOLYL ACRYLIC ACID

METHYL - CINNAMIC ALDEHYDE

PHENYL METHACRYLIC ALDEHYDE

METHYL CINNAMYL KETONE v Benzyl-idene acetone

METHYL CINNOLINE CARBOXYLIC ACID

 $C_{10}H_8N_2O_2$ is $C_8H_3(CO H)$ CMe CH N=N[6 280°]

Small tables or fine needles Sol acetic acid, sl sol hot alcohol and hot water, insol cold water Dissolves both in aqueous acids and alkalis, forming easily soluble salts Obtained, as a yellow pp, by adding NaNO, to a cold solution of the hydrochloride of amido propenyl benzoic acid C₆H₃(CMe CH | (NH₂)CO.H(1 2 4], very probably di azo-propenyl-benzoic acid C₆H₃(CO₂H) < CMe CH | s first formed, which then splits off H O (Widman, B 17, 722)

METHYL-GITRACONIC ACID C₆H_xO₄, [100°] A product of the dry distillation of methyl-paraconic acid (Frankel A 255, 25) Long needles (from CHCl₃) Reduced by sodium amalgam to ethyl succinic acid — CaA" aq — BaA" 4aq —

Ag 4'

METHYL COCAINE C₁₈H₂₂NO, [47°] Extracted from synthetical cocaine (cf vol 11 p 230), in which it occurs in very small quantity (Luebermann a Giesel, B 23, 508, 926) An oil, which crystallises after standing some hours Ppd. by Na.CO, from its salts Very sol ether, chloroform, benzene, and ligron It can be separated from ordinary cocaine by means of its nitrate A 54 p c solution of the hydrochloride in a 2 dm tube gave a rotation of +45° By heating with water it is not so easily decomposed as ordinary cocaine By boiling with hydrocia acid MeI is split off By hydrochloric acid it is split

ip finally into methyl alcohol, benzoic acid, and methyl ecgonine hydrochloride This reaction is also more difficultly brought about than with ordinary cocaine. Methyl cocaine appears to be identical with 'dextro cocaine,' a body got by heating the methyl ether of dextro ecgonine with BzCl (Einhorn a Marquardt, B 23, 468)

Salts -B'HCl [210°] needles or columns forming rosettes (from hot alcohol), much less soluble than the hydrochloride of ordinary cocaine —Sulphate plates, v sol water, sl sol alcohol —Nitrate crystals, al sol water — Platino chloride (C18H23NO, HCl)2PtCl48 glittering yellowish needles (from hot water) — Auro-chloride C18H28NO4HClAuCl3 [1480]. needles, melts under water to a yellow oil

METHYL CODEINE C₁₈H₂₈NO, 2 e C₁₈H₂₉MeNO, or C₁₇H₁₇Me₂NO, [118 5°] $[a]_{\rm p} = -209^{\circ}$ in a 4 p c solution (in 97 p c alcohol) at 15° Formed by boiling code me methylo iodide C_{1s}H₂₁NO₂MeI with potash, and extracting with benzene (Grimaux, A Ch [5] 27, 276, Hesse, A 222, 218) Anhydrous prisms (from alcohol or ether), or hydrated crystals (contain- $\log aq$) (from water) Insol water, v e sol hot alcohol, m sol ether Its solution in conc H_2SO_4 is violet, but becomes blue on heating Boiling Ac₂O forms a compound C₁,H₁₄O₃ [131°] Its hydrochloride forms a brown solution in H₂SO₄, which becomes violet on warming, and finally blue on exposure to the air -B'HCl 2aq V e sol alcohol, sl sol needles S 9 at 18°

NaClAq —B'2H2PtCle aq Acetyl derivati derivative C₁₃H₁₆AcMe₂NO₃ [66°] Formed by heating methyl codeine with Ac₂O at 85°, adding aqueous NH, and extracting with ether (Hesse, A 222, 222) Glittering tables (from ether), v sol alcohol and ether, sl sol water, insol KOHAq Alcoholic potash Alcoholic potash forms potassium acetate and methyl codeine -satiny plates —(C₁₇H₁₆AcMe₂NO₃)₂H₂SO₄ 8aq

(a) Methylo-rodide C19H23NO3MeI 2aq prisms, formed at once on dissolving methyl codeine in a mixture of MeI and methyl alcohol

(B) - Methylo - rodide C₁₉H₂₃NO₃MeI Slender crystals, formed by boiling the preceding with aqueous NaOH, and ppg with KI It is less soluble in water than its (a) isomeride Ag₂SO₄ forms (C₁₉H₂₃NO₂Me)₂SO₄, crystallising

ın plates

C₁₉H₂₃NO₃MeCl (a)-Methylo-chloride From the (a)-10dide and AgCl Amorphous With platinic chloride it yields a yellow floccu lent pp of (C₁₈H₋₃NO₃MeCl),PtCl, 8aq With Ac₂O it yields C₁₈H₋₂₂AcNO₃MeCl 2½aq, which crystallises in long satiny needles, v e sol alco hol, sl sol cold water Its platinochloride (C19H22AcNO,MeCl)2PtCl, 4aq 1s a yellow crystalline pp

(B)-Methylochloride C19H23NO2MeCl 3sq Radiating crystalline mass, v sol water and alcohol With cone H₂SO₄ it gives a purple colour With platinic chloride it yields an orange pp of small needles of the platinochloride (C₁,H₂₂NO₂MeCl)₂PtCl₄ aq With Ac₂O it yields amorphous C₁,H₂₂AcNO₂MeCl, which forms (C₁,H₂₂AcNO₃MeCl)₂PtCl₄ Saq, a yellow powder

Methylo-hydroxide *C19H28NO3MeOH. Formed from the (B) methylo sulphate and Colourless plates, insol ether, v sol baryta Strongly alkaline in reaction Conc alcohol H₂SO, forms a blue solution Gives off trimethylamine when strongly heated

METHYL COLCHICINE C23H27NO6 1 e C₁₈H₉(OMe)₂(NAcMe) CO₂Me Occurs in the mother liquor from which the compound of col chicine with chloroform has separated (vol 11 p 234) Decomposed by boiling dilute HCl into methyl chloride and methyl colchicein C13H9(OMe) (NAcMe) CO2H (Johanny a Zeisel,

M 9, 871 DI METHYL-COLCHICINIC ACID v D

methyl derivative of Colchicinic acid

Tri methyl-colchicinic acid C19H21NOs i e $[150^{\circ}]$ $\mathbf{C}_{15}\mathbf{H}_{9}(\mathrm{OMe})_{8}(\mathrm{NH}_{2})\mathbf{CO}_{2}\mathbf{H}$ Formed by the action of HCl on colchice $(q \ v)$ Forms a platinochloride B', H.PtCl, 2aq On warming with acetic anhydride it yields colchicein C₁₅H₉(OMe),(NHAc) CO₂H With MeOH it forms an addition product C₁₉H₂₁NO₅2MeOH warming with MeOH, methyl iodide, and so dium it yields 'tri methyl colchidimethinic acid' $C_{15}H_{s}(OMe)_{s}(NMe_{s})CO_{s}H$ [125°] The methyl ether of this body forms an iodomethylate $C_{22}H_{36}NO_{5}Iaq$ (Johanny a Zeisel, M 9, 877)

METHYL-CONIINE v CONIINE METHYL-COUMARIC ACID v Methyl deri vative of Coumaric acid

Di-methyl di coumaric acid so called v Di METHYL DI-COUMARIN

METHYL COUMARILIC ACID C, H,O, te C₆H₄<0Me CO₂H [126°] Formed by the action of dilute KOH upon the methyl derivative of exo bromo coumaric acid (Perkin, C J 39, Needles (from CS2)

(β) Methyl coumarilic acid C₁₀H₂O₃ ι e $C_6H_4 < CMe > CCO_2H$ [189°] Formed by saponifying its ethyl ether with alcoholic potash (Hantzsch, B 19, 1290) Feathery needles (from dilute alcohol) Decomposed by heat into CO₂ and (β) methyl coumarone — KA'aq needles — NH₄A'aq needles (from water) —

BaA', 3aq —AgA' minute prisms Ethylether EtA' [51°] (290°) Formed by the action of sodium phenylate NaOC, H, upon chloro aceto acetic ether, the resulting phenoxy aceto acetic ether being condensed by

cold conc H₂SO₄ (Hantzsch)

A mide C₈H₄(CH₉)O CO NH₂: needles (Hantzsch, B 19, 2401)

Di-methyl-coumarilic acid C11H10O3 2 &

C₆H₃(CH₃) CC(CH₃) CCO₂H Di methyl coumarone-a carboxylic acid [225°]

Formation —1 By the action of hot alcoholic KOH upon brome di methyl cumarin

C₆H₃(CH₃) CGr O____CO -2 By saponification of the ethyl ether obtained by the reaction of

sodium p cresol and chloro aceto acetic ether Properties — Short prisms or tables On heating the sodium salt with lime di methylcoumarone is obtained

[55°], Ethyl ether A'Et 728 mm) (Hantzsch a Lang, B 19, 1299). Reference — Coumarilio acid and Oxy-

METHYL COUMARIN v Anhydride of Oxy-PHENYL CROTONIC ACID

m β D1 methyl coumarin C11H10O2 2.6.

by the action of H.SO, on a mixture of acetoacetic ether and p cresol (Pechmann a Dusberg, B 16, 2127, Pechmann a Cohen, B 17, 2187) Long colourless needles

Reference —Brom. DI METHYL COUMARIN DI methyl di coumarin C₁₄H₁₀O₄ 2 e

C.H (CMe CH) Formed by dissolving resor cin (1 mol) and acetoacetic ether (2 mols) in

cin (1 mol) and acetoacetic ether (2 mols) in cone H_2SO_4 , yield 10 pc Microcrystalline white powder V sl sol boiling alcohol, nearly msol water, ether, chloroform, benzene, &c Dissolves in aqueous alkalis to a yellow solution, from which acids ppt di me thyl di coumaric acid $C_4H_2(OH)_2(CMe\ CH\ CO_2H)_2$ The latter forms a white powder, sol alcohol, at 140° it is completely reconverted into the anhydride (Hantzsch a Zurcher, B 20, 1328)

Tri methyl tri coumarin C18H12O6 26

C. (CMe CH Formed by dissolving phloro

cO—CO/s gluein (1 mol) and acetoacetic ether (3 mols) in conc H.SO₄, the yield is less than 10 pc. Amor phous powder. Insol all solvents. Dissolves in aqueous alkalis to a yellow solution, from which acids ppt tri methyl tri coumaric acid. C₆(OH)₄(CMe CH CO,H)₃, whose sodium salt is Na₃A" baq (Hantzsch a Zurcher, B 20, 1330)

(β) METHYL COUMARONE C₉H₅O ι e

Constant Country Count

Di methyl coumarone $C_{10}H_{10}O$ is $C_{10}H_{10}CH_{10}O$ is $C_{10}H_{10}CH_{10}CH_{10}$ at 728 mm) indifferent oil. Formed by distilling the sodium salt of di methyl coumarilic acid (di methyl coumarone a carboxylic acid with lime (Hantzsch a. Lang, B 19, 1300)

METHYL - CREOSOL v Methyl ether of

METHYL CROTONIC ACIDS v Angelic acid and Tiglic acid

METHYL ISOCROTYL OXIDE v Sec ISO BUTENYL ALCOHOL

METHYL CUMARIN v METHYL COUMARIN METHYL - CUMAZONIC ACID C₁₂H₁₃NO,

• $e \ C_e H_3(CO_2H) \left\langle \begin{array}{c} CMe_2 \ O \\ N-CMe \end{array} \right\rangle$ (?) [218°].

Formation —1 By boiling (3 4 1) amidooxypropyl benzoic acid with acetic anhydride 2 By boiling acetyl amido oxypropyl benzoic acid with HCl —3 By boiling acetyl amido propenyl benzoic acid with HCl Small colour less trimetric tables V sol alcohol, insol water Its N is tertiary

Reactions -By reduction with sodium-

amalgam it yields the acetyl derivative of amido cuminic acid

Salts — A'H,HClx very soluble white needles — (A'H,HCl)₂PtCl₄ tables, cubes, or prisms — A'H,H₂SO₄ aq very soluble white silky needles (Widmann, B 16, 2576)

METHYL-CUMENE v CYMENE

METHYL - ψ - CUMIDINE $C_{10}H_{13}N$ to $C_{4}H_{4}(CH_{1)}$, v - MHMe [44°] (237°) Formed by methylation of solid cumidine [63°] — By-H.Cl.-ptCl. sparingly soluble needles (Hofmann, B 15, 2896)

Di methyl - ψ cumidine $C_sH_2(CH_1)_3$ NMe₂ (222°) Oil Formed by methylation of solid cumidine [63°] — B'₂H₂Cl₂PtCl₄ (Hofmann, B 15, 2897)

Methylo - todrde C.H (CH.,),NMe,I Prisms Yields (C.H.,(CH.,),NMe,Cl),PtCl, METHYL CUMYLETHYL KETONE

METHYL CUMYLETHYL RETONE
C,H, C,H, CH, CH, CH CH, CO CH, Cummyl acetone
(260°-265°) Is one of the products of the
action of NaOEt and cuminyl chloride on aceto
acetic ether (Widmann, B 22, 2271) Colourless
liquid, with fragrant odour Is not acted upon
by NaOBr Oxidised by KMnO, to cuminic
acid

Oxim C₁H, C₆H, CH₂ CH₂ C(NOH) CH, [57°] Long shining prisms (from ligroin) METHYL CUMYL KETONE

CH₃ CO C₄H₄Pr [1 4] (253°) SG 15 9755 Formed by the action of AcCl on cymene in presence of AlCl₃ (Widmann, B 21, 2225)

Oxim CH, C(NOH) C,H,Pr [71°] Four-

sided tables (from petroleum ether)

Phenyl hydrazide

CH, C(N,HPh) C,H,Pr [82°] Colourless thick six sided tables (from petroleum ether)

METHYL CYANAMIDE v Cyanamide in the article Chanic acids

METHYL CYANATE v CYANIC ACIDS
METHYL-GYANETHINE v CYANETHINE
METHYL CARBIMIDE is Methyl isocyanate
v Cyanic acids

METHYL CYANIC ACID v CYANIC ACID METHYL CYANIDES v Acfionitrile and METHYL CARBAMINE

Di methyl di cyanide C₁H_eN i e NH CMe CH₂CN oi NH₂CMe CH CN [53°] V D 425 Formed by the action of dry sodium on acetonitrile dissolved in ether Methane is evolved in the reaction, and the product is decomposed by water (Holtzwart, J pr [2] 38, 343, 39, 240) White needles, v sol ether, alcohol, chloroform, and benzene, m sol water, sl sol petroleum ether

Reactions—I Boiling water liberates ammonia forming $C_8H_8N_2O$, a body which is converted by PCl₈ into crystalline $C_8H_8N_1Cl_1$ [175°], which, on recrystallisation from water, becomes $C_8H_4N_2$ —2 Acetyl chlorade forms a compound $(C_1H_4N_2)_1CH_3COCl$, which on decomposition by water yields $C_8H_8N_8$, crystallising in beautiful white needles [223°]—3 Warm dilute (25 r c) HClAq forms NH₄Cl and an oil which has the composition of cyano acetone—It solidifies to a glassy fhass, carbonises above 230°, and forms with phenyl hydrazine a condensation product [97°]

Tri-methyl tri-cyanide v Cyanmethinf METHYL-CYANO FORMAMIDE v Methylamde of Para-Cyanofobmic acid METHYL-CYANO-SUCCINIC ETHER

C₁₀H₁₈NO₄ is CO₂Et CH₂ CMeCy CO₂Et An oil formed by treating cyano succinic ether with Na and MeI successively (Barthe, C R 108,

s-Di-methyl cyano-succinic ether C11H17NO4 te CO2Et CHMe CMeCy CO2Et (273°) 245 10577 A product of the action of alcoholic KCy on a bromo propionic ether (Zelinsky, B 21, 3164) Formed also by adding α bromopropionic ether to cyano-propionic ether mixed with KCy (Z)
METHYL CYANURIC ACID v Cyanuro

acid in the article Cyanic acids

METHYL CYMYL KETONE C12H16O 26 (247°) An oil, CH, CO C,H,Me C,H, [2 1 4] formed by the action of AcCl on cymene in presence of AlCl. (Claus, B 19, 233)

METHYL-DAMBOSE v BORNESITE, vol 1.

p 524

D1-methyl-dambose v DAMBONITE METHYL-DAPHNETIN v DAPHNETIN

METHYL DECYL KETONE C12H24O 18 CH, CO C₁₀H₂₁ [21°] (247°) Formed by distilling a mixture of barium acetate and barium hendecoate (undecylate) (Krafft, B 15, 1708) Yields acetic and decoic acids on oxidation

METHYL - DESOXYBENZOIN BENZYL KETONE

Dimethyldesoxybenzoin v Benzyl xylyl

METHYL DODECYL KETONE C,4H 8O 16

(206° at 100 mm) CH₂ CO C₁₂H₂₅ [34°] (Formed by distilling barıum tridecoate $(C_{13}H_{23}O_2)_2$ Ba with barium acetate (Krafft, B 15, 1708) Yields lauric and acetic acids on oxidation

METHYL c-DURYL KETONE C12H16O 16 (259°) CH, CO C₆HMe₄ [1 2 3 4 5] From c durene, AcCl, and AlCl, (Claus a Fohlisch, J pr [2] 38, 230) Oil

Phenyl hydrazide [129°] Laminæ Isomerides v DURYL METHYL KFTONES

METHYL-ECGONINE C10H17NO3 A product of the action of HCl on methyl cocaine, the resulting methyl ecgonine hydro chloride being decomposed by Ag₂O (Liebermann a Gresel, B 23, 510) May be crystallised from methyl alcohol containing a trace of water Extremely sol water, insol absolute alcohol, v sl sol absolute MeOH Decomposed by fusion A 9 6 p c solution of the hydrochloride exhibits $\alpha = +2^{\circ}$ —B'HCl [236°], needles (from methyl alcohol ether) —B'HAuCl [220°], lemon yellow needles

Benzoyl derivative Hydrochloride of hydrochloric acid on methyl cocaine [47°], the base being just dissolved in HCl and then heated $\frac{1}{2}$ hour at 90° Glassy columns (from hot water) The base is not ppd by carbonate of soda —Aurochloride C₁₇H₂₁NO₄ HCl AuCl₃ The nitrate is v sl sol water

METHYLENE The radicle CH2, which is not known to exist in the free state

Dimethylene C2H4 we CH, CH, 18 called ETHYLENE $(q \ v)$

CH₂ Trimethylene CaHate CHat HFp -8470 H.F v. -4630

when trimethylene bromide CH2Br CA2 CH3Br (140 g) is boiled with sodium (5 g) The contents of the flask become pasty, but still contain much of the bromide (120 g), which can be mostly recovered by filtration (Freund, J pr [2] 26, 367) It is also formed by heating tri methylene bromide with zinc dust and 75 pc alcohol (Gustavson, J pr [2] 56, 800) Trimethylene burns with a bright flame and smells like butylene

Reactions -1 Trimethylene is readily ab sorbed by fuming HI The product is n propyl iodide, whereas propylene gives iso propyl iodide Trimethylene is very slowly absorbed by bromine, the product is trimethylene bromide (165°) Propylene is readily absorbed, forming propylene bromide - 3 Conc H2SO, forms liquid hydrocarbons, and on diluting and distil ling n propyl alcohol is got (G) -4 KMnO. does not oxidise it (Wagner, B 21, 1230)

References -TRIMETHYLENE CARBOXYLIC ACIDS, TRIMETHYLENYL METHYL KETONE, and PHENYL TRIMETHYLENYL KETONE

Tri methylene is a term also applied to the divalent radicle CH, CH, CH,

Tetra methylene is a term applied to the ring

CH, CH, , and it is also used to denote the group ĊH, ĊH,

CH. CH, CH, CH Pentamethylene is a name used to denote CH, CH, CH, CH, CH, CH

Hexamethylene is benzene hexahydride Ac cording to Baeyer (A 258, 156), it should be regarded as lying entirely in one plane

METHYLENE ACETATE v Acetyl der iva tive of Formic orthaldehyde, vol 11 p 570

TRIMETHYLENE ACETO ACETIC ACID, so

called, v vol 1 p 24
METHYLENE DIAMINE Di benzoyl de rivative CH (NHBz), [221°] S 47 at 14 5°, 63 at 22°, Hipparaffin S (alcohol)

Formation -From hippuric acid, PbO2 and HNO₃ or H SO₄ (H Schwarz, A 75, 201, Stt. W 77, 11 762, J Maier, A 127, 162, kiaut a Y Schwarz, A 223, 40)

Preparation - From benzonitrile (15 g). methylal (6 g) and conc H₂SO₄ (100 g) (Hepp a Spiess, B 9, 1424)

Properties —Long white felted needles (from

alcohol), v sol CS₂, ether, and chloroform

Reactions —1 Dissolves unchanged in conc H₂SO₄, and in fuming HNO₃ -2 On distillation some passes over unchanged along with benzoic acid -3 Not affected by bromine -4 Boiled for some time with dilute (32 p c) H2SO4 it gives formic aldehyde, NH, and benzoic acid -5 Heated in sealed tubes with dilute HCl it yields benzamide and formic paraldehyde

Trimethylene diamine C,H,,N, i e NH,CH,CH,CH,NH, (c 140°) Formed by heating trimethylene bromide (1 mol) and NH, (20 mols) in alcohol for 10 hours at 100° liquid is decanted from NH, Br and evaporated, treated with KOH and distilled (Fischer a Koch, B 17, 1799, Lellmann a Wurthner, A 228, Colourless mobile liquid, easily miscible 227) with alcohol, ether, and benzene Fumes in This gas is formed moist air, combining with water to form a hydrate Readily takes up CO₂ becoming solid Condenses with benzoic aldehyde forming $C_3H_4(N \text{ CHPh})_2$ Phenanthraquinone forms C_8H_1,NO_2 a yellow powder, melting above 250° Benzil forms $CH_2 < CH_2 \ N \ CPh > a$ transparent

vitreous mass [c 76°]

Salts —B"H₂Cl₂ Easily soluble prisms — B"H₂Cl₂PtCl₄ Orange prisms — B"(HSCN)₂ [102⁶] At 140° it is partially decomposed into trimethylene thio-urea and NH₄SCN — B"H₂Br₂.

Diacetyl derivative C₂H₆(NHAc)₂ [79°] White needles, v e sol water, v sol alcohol, chloroform, sl sol benzene, insol ether, petro

leum ether (Strache, B 21, 2364)

Dibensoyl derivative C,H₆(NHBz)₂ [148°] White orystalline powder, insol water, m sol benzene, v sol alcohol and chloroform On heating in a stream of HCl the product is C,H₆
NH
OPh, an only base which slowly becomes crystalline and forms crystalline salts (Hofmann, B 21, 2337)

Oxalyl derivative CH2 CH2 NH CO

A sparingly soluble white powder, formed on mixing trimethylene diamine with an alcoholic solution of methyl oxalate It does not melt at 250°

Derivative — V OXY TRI METHYLENE DIAMINE Trimethylene di nitro di-amine C,H₄N,Q₄ ie NO, NH CH₂ CH₄ CH₂ NH NO, [67°] Formed by heating C,H₆(N(NO,) CO,M₉), (v Tri METHYLENE DICARBAMIC ACID) with aqueous ammonia (Franchi mont a Klobbie, R T C 7, 343) Short thick prisms (from water or alcohol), v sol water and alcohol, less sol ether and chloroform Boiled with dilute (2 p c) H₂SO₄ it evolves N₂O It has no acid reaction, and easily forms metallic derivatives

Tetra methylene diamine $C_1H_{12}N_1$ is NH_2 CH_2 CH_3 CH_4 CH_4 CH_5 CH_7 NH_2 CH_7 CH_8 CH_9 CH_9

NH₂ CH₁ CH₂ CH₂ NH₂ [24] (159°) Obtained by reducing ethylene cyanide in alcoholic solution with sodium (Ladenburg, B 19, 780) Identical with the ptomaine 'putrescine' (cf. L. Brieger, 'Die Ptomaïne,' Berlin, 1885–1886, 1, 43, 3, 101) and also with a base obtained from a morbid urine (Udranszky a Baumann, B 21, 2938). Strong base, smelling like piperidine Solutions of its salts give a crystalline pp with iodine dissolved in KIAq but no pp with HgCl₂ or KCdI₄. When shaken with aqueous NaOH and BzCl it gives a crystalline pp of the dibenzoyl derivative Methyl chloroformate ClCO₂Me forms (CH₂)₄(NH CO₂Me)₂ which crystallises in flattened needles [128°], sl sol cold water, and is nitrated by HNO₃, yielding (CH₂)₄(N(NO₂)CO₂Me)₂ which crystallises from ether and melts at 62° (Dekkers, R. T. C. 9, 97).

Salts —B"H₂Cl₂. Plates (from alcohol) — B"H₂PtCl₆ Needles —P10rate Thin yellow needles — Aurochloride [210°] Minute thread like needles, v sol hot water (Ciamician

a Zanetti, B 22, 1978)

D1-bensoyl destructive C,H,(NHBs),[175°] (U a B), (178°] (C a Z) Plates, insol water, almost insol ether, v sol hot alcohol
May he sublumed

May be sublimed

Tetra-methylene-di-nitro-di-amine C₄H₁₂N₄O₄
i.e. (OH₂)₄(NH NO₂)₃. [168°] Got by heating

Voz. III.

(CH₂)₄(N(NO₂)CO₂Me)₂ with cone NH₂Aq at 100° and ppg by HOAc (D) Small hard crys tals (from water)

Penta methylene diamine C₃H₁₄N₂ te NH₂ CH₂ C

distillation into NH₃, HCl, and piperidine
Salts—B"H₂Cl₂—B"H₂PtCl₃ Thick orange
prisms (from water), m sol cold water—Per
iodide Almost black crystals (from alcohol)—
B"H₂Cl₂ 3HgCl₂ Crystals (from hot water)
(L)—B"H₂Cl₂ 4HgCl₂ Crystals (from alcohol)

(B)

Dr acetyl derivative
CH₂(CH₂ CH₂ NHAc)₂ Small needles (from al cohol) May be distilled

Di benzoyl derivative

CH₂(CH₂CH₂NHBz), [130°] (above 360°) Ppd by adding aqueous NaOH and BzCl to a solution of the base (Udranszky a Baumann, B 21, 2744) Long needles and plates, v sol alcohol, m sol ether, insol water Not affected by hot dilute acids or alkalis

Penta methylene di nitro di amine
CH₂(CH₂ CH₂ NH(NO₂))₂ Formed by treating
CH₂(CH₂ CH₂ N(NO) CO₂Me)₂ with aqueous
ammonia (Franchimonta Klobbie, R T C 7,
343) Small oblong plates (from chloroform),
v sol water and alcohol, sol ether, sl sol
CHCl₂ When boiled with dilute (2 p c) H₂SO₄
it evolves N₂O

Di nitroso penta methylene tetramine (so called) $C_3H_{10}N_4O_2$ is $C_3H_{10}N_4(NO)_2$. [207°] (G), [203°] (M) Formed by the action of nitrous acid on 'hexamethylene tetramine' (Griess, B 21, 2738, Mayer, B 21, 2888) Needles (from alcohol), v sol hot alcohol, m sol chloroform, insol ether Not affected by boiling with zincdust Dilute HCl decomposes it into nitrogen, ammonia, and formic aldehyde

Hexa methylene tetramine (so called)

C₃H₁₂N₄ Hexamethyleneamne [189°] S

(alochol) 7 Mol w 115 (by Raoult's method)

(calc 140) (Tollens a Mayer, B 21, 1566)

Formed by passing dry NH₃ over heated trioxy methylene (formic paraldehyde) (Butlerow,

A 115, 322, Z [2] 5, 278) Prepared by dissolving methylal in dilute H₂SO₄, and distilling
the product with steam into a receiver containing
ammonia (Wohl, B 19, 1842)

Properties—Rhombohedra (from alcohol), v sol water, chloroform, and CB. May be sublimed Scarcely attacked by sodium-amalgam Acts nutritiously upon algae (Loew a Bokorny, J. pr [2] 86, 272)

Reactions, -1. Split up by boiling dilute

acids into formic aldehyde and ammonia -2 MeI at 190° forms NMe₄I (Tollens, B 17, 656) 3 Sodrum nitrite $(2\frac{1}{2} \text{ pts})$ added to a solution of the base (1 pt) in dilute HCl at 0° forms 'tri methylene tri nitrosamine' CaHaNaOa, which crystallises from alcohol in needles or prisms [106°], and is split up by warming with dilute acids into nitrogen and formic aldehyde Ιt exhibits Liebermann's reaction When acetic acid is added gradually to a solution containing hexamethylene tetramine and sodium nitrite there is formed the so called di nitioso penta methylene tetramine (v supra), which is much less soluble in the usual menstrua than the tri methylene tri nitrosoamine

Salts -B"H₂Cl₂ (dried at 100°) prismatic needles, v e sol water, sl sol alco hol -B"2H2PtCl, 4aq -B"23AgNO3 Whitecrys talline pp, formed on adding AgNO, to an aqueous solution of hexamethylene tetramine (Pratesi, G 13, 437) Sl sol cold, m sol hot, water, with partial reduction to silver

Methylo rodide B"MeI [190°] water, sl sol alcohol, insol ether, chloroform, and CS₂

Ethylo rodide B"Etl [133°]
Methyleno rodide B"CH₂I₂

[165°]

Di-bromide C₆H₁₂N₄Br₂ Insol ordinary

solvents (Legler, C C 1888, 1604)

Tetrabromide C, H₁₂N, Br. Red crystals, obtained by the action of bromine vapour on hexamethylene tetramine (Horton, B 21, 1999)

Decomposed by boiling water $Di\ iod\ id\ C_eH_{12}N_4I_2$ Obtained by adding an alcoholic solution of iodine to an aqueous solution of the base Crystalline, v sl sol

Tetra rodide C_eH₁₂N₄I₄ Obtained when sess of rodine is used Minute brown plates, excess of rodine is used sol acetone, CHCl_s, and CS₂ Decomposed by boiling water

METHYLENE DI-ISOAMYL DIOXIDE v FORMIC ALDEHYDE

METHYLENE - ANILINE $(\mathbf{C},\mathbf{H},\mathbf{N})_x$ Anhydro formaldehyde aniline $(CH_2 NPh)_x$ [138°] Formed by mixing aniline and crude formic aldehyde in the cold (Tollens, B 17,657, 18, 3309, Kolotoff, Bl [2] 43, 112) White silky crystals, v sol chloroform and benzene, sl sol alcohol, insol water Decomposed by boiling

with water or alcohol —B', H, PtCl, Methylene-aniline C, H, N Formed, together with di phenyl methylene diamine and the preceding body by the action of formic aldehyde on aniline (Pratesi, G 14, 355) Minute crystals, decomposed by heat V sl sol alcohol

Methylene-di-aniline v DI-PHENYL METHYL-ENE DIAMINE

METHYLENE-DIBENZYLAMINE O18H18N e CH₂(NH CH₂Ph)₂ [46°] (c 227°) Formed by the action of methylene chloride on benzyl amine at 100° (Kempff, A 256, 220) Rhombie prisms, insol water, v sol absolute alcohol and ether

Salts—C₁₅H₁₈N₂2HOl [242°] Colourless monoclinic plates—B"2HBr silky plates— B"2HI monoclinic plates (from benzene), sl sol water and alcohol -B"H2SO42aq colourless prisms —B"2H,PO, [c 230°] Needles -B"H_Cl_PtCl. monoclinic plates —Aurochlor-

ide B"H₂Cl₂AuCl₂ golden yellow needles,—Oxalate B"(H₂C₂O₄)₂ [c 134°]—Picrate Oxalate $B''(H_2C_2O_4)_2$ [o 134°]—Piorate $B''(C_6H_2(NO_3)_2OH)$, not stable in a hot solution, sl sol alcohol, and water

METHYLENE BLUE v TETRA METHYL DI AMIDO IMIDO DI PHENYL SULPHIDE

TRIMETHYLENE BROMHYDRIN \boldsymbol{v} Bromo PROPYL ALCOHOL

Formed by adding bromine to methylene iodide under water (Butlerow, A 111, 251, Henry, A Ch [5] 30, 266) Formed also by heating methyl bromide with bromine at 250° (Steiner, B 7, 507) Found among the bromides obtained by passing into bromine the products got by passing ethylene through a red hot tube (Norton a Noyes, Am 8, 362) Colourless mobile liquid, insol water, sol alcohol and ether Converted by PCl₅ at 190° into CCl₄ and CBr₄ (Holand, A 240, 230) When heated with 18 vols water and excess of PbO at 145° it yields ethylene glycol, traces of ethylene oxide, and PbBr₂ (Jeltekoff, B 6, 558) Slowly converted by SbCl, into methylene chloride Potassium phenylate KOC₆H₅ yields CH (OC₆H₅)₂
Trimethylene bromide v Di Bromo Propane

Tetra-methylene bromide C₄H₈Br₂ (189°) Formed from ethylene cyanide by successive conversion into tetra methylene diamine and CH₂(OH) CH₂ CH₂ CH₂(OH), the glycol being then treated with HBr (Gustavson a Dem janoff, J pr [2] 39, 542) The yield is small

Penta methylene bromide C₅H₁₀Br, reCH₂(CH₂CH₂Br)₂ (205°) Formed by satu rating the corresponding di oxy pentane (derived from tri methylene diamine) with HBr (G a D)

METHYLENE BROMO-IODIDE v Bromo IODO-METHANE

METHYLENE-TETRA-BUTYL-DIAMINE CH₂(N(C₄H₉)₂)₂ (250°) Obtained by distilling trimethylene oxide with dissolutyl amine (Ehrenberg, J pr [2] 36, 124) - B"H₂PtCl₆ [198°] Pale yellow powder — Aurochloride [c 195°] — B'CS₂ [54°] METHYLENE DI ISOBUTYL DIOXIDE v

Di isobutyl ether of Formic orthaldfhydf, vol

n p 571 METHYLENE CAFFEIC ACID v vol 1 p 659

TRIMETHYLENE DICARBAMIC ACID *CH₂(CH₂ NH CO₂H)₂

Methylether CH2(CH2 NH CO2Me), [75°] Formed by treating trimethylene diamine with methyl carbonate (Franchimont a Klobbie, R. T. C. 7, 343) Oblique rhombic plates V sol water, alcohol, and CHCl,, m sol ether, v sl sol benzene and light petroleum Pure HNO, yields a dinitro-derivative forming tufts of needles or prisms from alcohol [90°], and this when treated with solution of ammonia gives tri-methylene dinitramine [67°

Ethyl ether CH₂(CH₂NH CO₂Et)₂ Tri methylene-drurethane [42°] (210° at 30 mm) When a solution of trimethylene diamine in alcohol and ether is added to an ethereal solution of chloro formic ether ClCO, Et, a pp of trimethylene diamine hydrochloride is formed, and the filtrate leaves on evaporation oily $C_3H_6(NHCO_2Et)_2$ (Fischer a Koch, A 232, 225) It crystallises after some time, and separates V sol ether, from ether in colourless prisms alcohol, and chloroform, sl sol ligroin, insol It dissolves in acids but is reppd by water alkalıs

Tetra methylene dicarbamic acid Methyl ether C4H8(NH CO2Me)2 [128°] Formed from tetra methylene diamine and ClCO2Me (Dekkers, R T C 9,97) Flattened needles, sol warm water Converted by HNO₃ into C₄H₈(N(NO₂) CO₂Me), which separates from ether in small brilliant crystals [62°], v al sel cold water, al sol ether, sol warm alcohol, and is converted by NH, Aq unto C₄H₈(NH NO₂)₂ [163°]

Pentamethylene dicarbamic acid Methyl ether CH₂(CH₂ CH₂ NH CO₂Me)₂ . [114°] Formed by treating penta methylene diamine with methyl carbonate Fine needles (from boiling water) V sol hot alcohol (Franchi mont a Klobbie, R T C 7, 343) Pure HNO3 gives a di nitro derivative, forming small bril liant prisms [37°], and this treated with aqueous ammonia gives penta methylene dinitramine [60°] together with methyl carbamate

TRIMETHYLENE CARBOXYLIC ACID CH₂ CH CO₂H or C,H,O, re

CH2 CH CH2 CO2H Isomeride of crotonic acid [19°] (183°) Formed by heating ethylene malonic acid (trimethylene dicarboxylic acid) at 210° (Roder, A 227, 24, Perkin, jun, C J 47, 817, B 17, 57) White crystals, m sol water Has a powerful odour and a burning taste -CaA', 6aq Needles, v sol water — BaA', 2aq Needles, v sol water — AgA' Small needles Gives off a low boiling oil on (from hot water) distillation

Ethyl ether EtA' (134°) Formed by digesting the Ag salt with an ethereal solution of EtI Volatile oil, with pleasant odour affected by bromine in the cold, and only slowly attacked when boiled with bromine, HBr being given off

Trimethylene (1 1)-di-carboxylic acid so called $C_4H_6O_4$ is e $C(CO_2H)_2$ or CH_2

CH₂ CH CH(CO₂H)₂ Vinaconic acid Ethylene malonic acid [141°] Obtained by saponification of its ether Colourless triclinic crystals, $a\ b\ c = 0\ 7712\ 1\ 8702$ Crystallises with aq (from water), v e sol water, v sol ether At 160° it begins to give off CO2, leaving trimethylene carboxylic acid It is not attacked by sodium When heated with bromine it gives off HBr slowly It combines, however, with HBr, forming bromo ethyl malonic acid (Per kin, O(J) 47, 814), and it combines with bromine when this is dissolved in chloroform (Fittig) Boiling dilute H₂SO₄ forms γ-oxy ethyl-malonic acid Alkaline KMnO₄ does not attack it (Buch ner, B 28, 704)

Salts-Ammonium salt Four-sided plates — CuA" aq Deep blue octahedra, sl sol hot water At 160° it becomes a light green powder -- BaA" Needles -- BaH, A", 4aq Pris matic needles -- PbA" (dried at 100°) Insol cold, al sol. hot, water -AgA" Needles, v. al

sol cold water, sl sol hot water -AgHA" Long

colourless needles (from water) Ethyl ether $\text{Et}_2\text{A}''$ (213°) VD 632 (calc 643) SG $\frac{15}{15}$ 10646, $\frac{25}{25}$ 10566 Formed by the action of ethylene bromide on sodiummalonic ether (Perkin, jun, C J 47, 812, B 17, 54, Fittig a Roder, A 227, 13) Oil Not attacked when successively treated with benzyl chloride and NaOEt (Perkin, jun, B 18, 1734)

Dibromide C3H4Br2(COOH), [110°] From tri methylene di carboxylic acid and Br in chlo roform (Fittig a Marburg, B 18, 3413)

Trimethylene (1 2)-di-carboxylic acid CH CO.H

CH₂CH CO₂H or CH₂ C(CO₂H) CH₂ CO₂H.

Allo tiacome acid [137°] (C a G), [139°] (B)
Formation—1 By heating its anhydride with water at 140° (Conrad a Guthzeit, B 17, 1187) -2 From sodium propane tetracarboxylic ether (CO2Et)2CNa CH2 CNa(CO2Et), by treatment with bromine, the resulting trimethylene tetracarboxylic ether being saponified, and the free acid heated to 230°, and then distilled under 16 mm pressure the oil which passes over at 170° to 180° is heated with water at 140° (Perkin, jun, B 19, 1056, Dressel, A 256, 197)

Properties — Prisms, v sol water, alcohol, and ether Not attacked by alkaline KMnO, or by sodium amalgam (Buchner, B 23, 705)

$$CH_2$$
 CH_2 CO O CH_2 CO O CH_2 CO CH_2 CH_2 CO CH_2 $CH_$

tricarboxylic acid CH₂C(CO₂H)₂ or possibly

CH_TC(CO₂H) CH(CO H)₂ at 184° to 190° for a long time (C a G) Needles, sl sol ether

Trimethylene (1 2)-di-carboxylic acid

CH CO,H [175°] \(\Gamma\)-cistrans-tri-methyl-∕¢н со³н

ene-12 di carboxylic acid Formed by saponification of the di methyl ether (Eduard Buchner, B 23, 705) Compact apparently rhombic crystals (from water), containing no water of crystallisation Grouped needles (from ether) Less sol water than the isomeric glutaconic acid, but Distils without splitting off more sol ether water Acetyl chloride forms no anhydride Not oxidised by permanganate in alkaline solution Not reduced by sodium amalgam Chloride of iron gives a weak red brown colour

Salts -The zinc saltis more sol cold than hot water It crystallises in nodular groups of needles A solution of the ammonium salt gives no pp with CaCl, and BaCl, but white crystalline pps with silver and lead salts By heating the silver salt a white body sublimes in needles, probably the anhydride

Do methyl ether C.H.(CO.Me), (205-215 at 718 mm) Formed by heating sorylodi azo acetic ether C.H.N.(CO.Me), for 40 minutes to 160°-185°. Saponified by boiling with aque ous potash.

28

Isomerides of trimethylene dicarboxylic acid v Itaconic, Citraconic, Mesaconic, and Gluta CONIC ACIDS

Trimethylene (1 1 2) tricarboxylic acid

∠ĆH CO₂H C_eH_eO_e ve CH₂ C(CO₂H)₂ CH₂ C(CO₂H) CH(CO₂H)₂ [184°] possibly

Formed by saponification of its ether, which is prepared by the action of as di bromo propionic ether on di sodio malonic ether (Conrad a Guthzeit, B 17, 1185) Its ether is also formed by the action of a bromo acrylic ether upon sodio malonic ether CHNa(CO₂Et)₂ (Michael, *J pr* [2] 35, 132, 351, *Am* 9, 121) Prisms (from water) At 184°... 190° it is split up into CO2 and the dicarboxylic acid or its anhydride

Tri-ethyl ether Et, A" (276°) 1 127 Colourless liquid Does not react with NaOEt and BzCl

Trimethylene (1 2 3)-tri-carboxylic acid

 $CH(CO_2H)$ (CO₂H)CH(or possibly `ĊH(CO₂H)

CO₂H CH C(CO₂H) CH₂ CO₂H [150°-153°] Formed by heating the tetra carboxylic acid (1 1 2 3) at 200° for a long time (Perkin, B 17, 1654, C J 47, 826) Colourless crystalline solid V sol water, alcohol, and acctone, sl sol benzene, chloroform, ligroin, and CS₂ On heating it yields a sublimate, probably of an an hydride

Salts —A"'Ag, white granular pp — A"'2Ca, crystalline pp, soluble in cold water, nearly insoluble in hot The cupric salt is a The beautiful light green pp, sl sol water Ba and Pb salts are white pps

Trimethylene (1, 2, 3) tri-carboxylic acid CH CO.H

co,H ch([220°] Obtained by CH CO2H

saponifying its methyl ether with alcoholic potash (Buchner, B 21, 2641) Small aggregates of needles (from ether), v sol alcohol and water, sl sol ether Not affected by bromine or by KMnO4 Its ammonium salt crystallises in plates

Methyl ether Me, A" $[61^{\circ}]$ (267°) at 732 mm , (224° at 180 mm) Obtained by distilling the compound of methyl fumarate with Needles (from alcohol or methyl diazo acetate water), v sol alcohol, ether, benzene, and petroleum-ether

Anhydride C,H,(CO,H) < CO > O [189°]

(265° at 75 mm) Obtained by distilling the acid under reduced pressure Small prisms, v sol water and alcohol, m sol ether Its Pb, Ba, and Ag salts are m sol water

Trimethylene (1,1,2,3) tetra-carboxylic acid

$$(CO_2H)_2O \begin{array}{c} CH(OO_2H) \\ \\ CH(CO_2H) \end{array} \quad \text{or} \quad \text{possibly}$$

(CO₂H)₂C C(CO₂H) CH₂ CO₂H [95°-100°] The tetra-ethyl ether of this acid is obtained by the action of di bromo succinic ether on di sodiomalonic ether (Perkin, B 17, 1652, C J 47, 824) Crystalline colourless solid V sol water, alcohol, ether, and acetone, sl sol ligroin and bonnene. Very strong acid The acid loses CO.

on heating to 200° giving the (1, 2, 3) tri carboxylic acid

Salts -A'Ag, white amorphous pp ---A''Ca2aq crystalline pp, more soluble in cold water than in hot

Tetra-ethyl ether AivEt. mm), thick colourless oil

Tri-methylene (1,1,2,2)-tetra-carboxylic

acid CH, (CO₂H), et [200°] Formed by saponifying the ethyl ether with alcoholic KOHAq (Dressel, A 256, 196) Large shining crystals (from water) When heated to 230° it gives off 2CO2 and H2O and is converted into the anhydride of trimethylene dicarboxylic acid, and from this the dicarboxylic acid itself can be ob-

tained by heating with water to 140° Ethyl ether $H_2C < \frac{C(CO_2Et)_2}{C(CO_2Et)_2}$ [43°]

(187°)Formed by the action of bromine on the disodium compound of propane tetra car boxylic ether (Dressel, A 256, 194, cf Perkin, B 19, 1056) Long needles, v sol ether, alcohol, CHCl, and benzene (D)

Tetra-methylene carboxylic acid C,H,O, te $CH_2 < CH_2 > CH CO_2H$ (191°) at 720 mm 8 G $\frac{15}{13}$ 1 0548, $\frac{25}{25}$ 1 0476 M M 5 048 at 18° μ_D 1 4403 at 26° Formed by heating tetra methylene dicarboxylic acid at 200°, CO₂ being given off (Perkin, B 16, 1795, C J 51, 8) Colourless oil, smelling like butyric acid, sl sol water, miscible with alcohol and ether Not attacked by bromine below 100°

Reaction -The calcium salt distilled with lime gives C₂H₄, H₂, CH₄, CO, di tetramethylenyl ketone, and tetramethylenyl methyl ketone (Colman a Perkin, jun, C J 51, 228, B 19, 3112)

Salts -AgA' sparingly soluble white pp -CaA'2 5aq

Ethyl ether EtA' (151°) at 720 mm (P),

(162°) (Freund, B 21, 2694) Chloride C₄H,COCl (143°) (F) tained by heating the amide with PCl's

Amide C₄H, CONH₂ [138°] (c 240°) Formed by heating the ammonium salt of the acid to 250° (Freund, B 21, 2694) Plates (from alcohol), v sol water, ether, chloroform, benz-May be sublimed Decomposed by treat ment with bromine and KOH

Natrale C.H, CN (150°) Formed by dis tilling the amide of tetra methylene carboxylic acid with phosphoric anhydride (Freund, B 21, 2696) Colourless oil, with pleasant odour Is converted into the amine by reducing with sodium and alcohol

Antlide C.H., CONHPh [111°] Formed by heating the amide with aniline until no more ammonia is given off (Freund) Long needles (from alcohol), sl sol hot water

Anhydride (C,H, CO)2O (160°) Formed by distilling the sodium salt with the chloride of the acid (F)

Tetra-methylene (1,1)-dicarboxylic acid $C_6H_6O_4$ to $CH_2 < \frac{CH_2}{CH_2} > C(OO_2H)_2$ [156°] From the ether (Perkin, O J 51, 4) Monoclinic crystals (from ether), a b c = 10324 1 1 1854, \$=98° 58'. V. sol. ether and bensene, nearly insol chloroform and ligroin, v sol water few degrees above its melting point it splits off CO, becoming tetramethylene carboxylic acid

Salts - AgaA" - CuA" aq - PbA" aq

BaA" aq

Ethyl ether Et₂A" (221°) at 720 mm SG § 10533, 25 10405. MM 9940 at 189° $\mu_{\rm D}$ 1 433 Formed from malonic ether, trimethylene bromide, and NaOEt (Perkin, B 16, 1793, C J 51, 2) Oil, smelling like camphor

Tetramethylene (1,2)-di-carboxylic acid CH2 CH(CO2H)

[130°] Formed by heating CH, CH(CO,H) the tetra carboxylic acid to 180°-200° (Perkin, B 19, 2042, C J 51, 22) Colourless feathery crystals (from water) V sol water, alcohol, and ether, more sparingly sol benzene and ligroin By alkaline KMnO4 it is oxidised to

oxalic acid Salts —A"Ag, heavy white pp —A"Bax sparingly soluble six sided transparent tables Diethyl ether A"Et2 $(238^{\circ}-242^{\circ})$,

colourless liquid CH2 CH CO

O [78°], colour-Anhydride CH, CH CO/

less crystals, easily soluble in alcohol, sparingly in ether and benzene Formed by heating the acid to 300° Reconverted into the acid by boil ing with water Heated with resorcin it gives a beautifully fluorescent condensation product

Tetramethylene (1,3) dicarboxylic acid

со н сн<^{СН}₂>сн со_лн Homortaconic Formed by boiling its ether with [171°] fuming HClAq (Markownikoff a Krestownikoff, A 208, 333) Prisms, v sol hot water and alcohol, sl sol ether May be sublimed not combine with bromine, but when heated with Br it gives off HBr and CO₂ It is not reduced by sodium amalgam Does not form an anhydride Does not unite with HBr or HI

Salts -PbA" laq Crystalline crusts -Ag₂A" Amorphous pp, not decomposed by

boiling water

Methylether Me.A" (220°)

Ethylether Et.A" (230°) Formed in very small quantity when CH, CH(OEt) CO, Et is prepared by the action of dry NaOEt on a chloro propionic ether (M a K)

Tetramethylene (1,1,2,2) - tetra - carboxylic CH₂ C(CO₂H)₂

. [145°-150°] Obtained by acid CH. C(CO2H)2

saponification of the tetra-ethyl ether, which is formed by the action of bromine upon the di sodio derivative of butane tetra carboxylic CH₂ CNa(CO₂Et)₂

ether (Perkin, B 19, 2041,

CH2 CNa(CO2Et)2

C J 51, 21) Colourless crystals Easily soluble in water, alcohol, and ether, more sparingly in benzene and ligroin It evolves CO2 at its melting point, and is converted into the di carboxylic acid

Tetramethylene (1,1,3,3) - tetracarboxylic acid Ethylether

(CO'Et)'CCCH'
CH'
CO'Et)'CCC'Et)' Formed by the action of methylene iodide on the di sodium de

rivative of propane tetra carboxylic ether in an alcoholic solution on the water bath (Dressel, A 256, 198) Colourless viscid oil, distilling with some decomposition between 220° and 250° at 15 mm

Pentamethylene dicarboxylic acid CH2-CH CO2H [160°]

CH,-CH CO,H

Preparation - Disodium pentane tetra carboxylic ether.

(CO,Et)2CNa CH2 CH2 CH, CNa(CO,Et)2 18 con- $CH_2-C(CO_2Et)_2$ verted by Br into CH. `CH₂---Ċ(CO₂Et)₂

yields pentamethylene tetracarboxylic acid on saponification, and this acid is decomposed by heat into CO2 and pentamethylene dicarboxylic This is purified by conversion into its ethyl salt (Perkin, jun, C J 51, 244, B 18, **3250)**

Properties - Nodules (from water) hot water, alcohol, and acetic ether, sl sol

Salts -Ag,A" Very stable white pp (° 250°) ,CH₂—CH CO. Ethyl sther Et.A" Anhydride CHA **℃H,**—ĊH CO∕

[64°-67°] Formed by heating the acid to 300° M sol alcohol and ether, sl sol CS₂, insol cold, but saponified by hot, Na₂CO₃Aq With resorcin and H.SO, it gives the fluorescein reaction

Penta-methylene tetracarboxylic acid

 $CH_2-C(CO_2H)_2$ Formed as above Sol. $^{\circ}CH_{2}$ — $C(CO_{2}H)_{2}$ ether

TETRAMETHYLENE CARBOXYLIC ALDE HYDE CH₂<CH₂>CH CHO (115°-117°) From

calcium tetramethylene carboxylate by distilling with calcium formate (Colman a Perkin, C. 51, 238) Oil, smelling like isobutyric aldehyde Gives a purple colour with rosaniline hydro chloride which has been bleached by SO2, reduces ammoniacal AgNO Aq, combines with NaHSO,, reacts with hydroxylamine and with phenyl hydrazine

TRIMETHYLENE CHLORHYDRIN CHLORO PROPYL ALCOHOL

METHYLENE CHLORIDE CH.Cl. D_{i} chloro methane Mol w 85 (418°) (Thorpe, C J 37, 195) S G $\stackrel{?}{_{\sim}}$ 1 3778 (T), $\frac{1}{15}$ 1 3377, $\frac{25}{35}$ 1 3220 MM 4 313 at 11 9° (Perkin C J\$\frac{95}{25} 1 3220 45, 527) (0°-10°) 001335, (0°-40°) 12 H C p 106800 (Berthe CES V 65 12 001416 lot a Ogier, Bl [2] 36, 68)

Formation -1 From chlorine and methyl chloride in sunlight (Regnault, A 33, 328, A Ch [2] 70, 377)—2 By the action of zinc dust and ammonia on chloroform, the yield being very small (Perkin, C N 18, 106) -8 By the action of chlorine on methylene iodide (Butlerow, A 107, 110, 111, 251, Z [2] 5, 276) — 4 By the action of AlCl, on the compound of Cl CO₂CCl, with Cl CO₂CH, (Hentschel, J pr [2]

Preparation - Aqueous HCl is cautiously added to a mixture of alcohol (5 vols), chloroform (1 vol), and sinc Sufficient heat is produced in the reaction to distil over much of the methylene chloride The product is fractionally distilled (Greene, C R 89, 1077, A Ph S 18, 847, C N 50, 75, A C J 1, 522)

Properties—Oil Like CCl₄ (but unlike CCl₄)

Properties—Oil Like CCl₄ (but unlike CH₃Cl and CHCl₅) it exerts a poisonous action when inhaled (Regnault a Villejean, C R 100,

1146

Reactions -1 Converted by ICl or ICl, into CHCl₃, and hexachloro benzene Converted by IBr into iodoform and di chloro di iodo methane (Holand, A 240, 234) Converted by IBr, into CBr, CHBr, and C2Br, -2 Heated with KI, iodine, and alcohol, it gives CH2I2, EtI, and alcohol (H) —3 Iodine at 200° gives methylene iodide (H) —4 Bromine at 170° forms iodide (H) -4 Bromine at 170° forms CHBrCl₂ (91°), and a little CBr₂Cl₂ [38°] (150°) (Arnhold, A 240, 204) -5 Alcoholic NaOAc forms CH₂(OEt)₂ and acetic acid (A) -6 Con verted by alcoholic NH, at 125° into so called hexa methylene diamine (Holand, A 240, 225) Aqueous ammonia at 140° forms NH₄Cl, methylamine hydrochloride and formic acid (André, C R 102, 1474) -7 Mixed with benzene it is converted by AlCl, into anthracene and other products (Friedel a Crafts, A Ch [6] 11, 264) 8 Water at 200° forms HCl, formic acid, MeCl, and MeOH (André) -9 With H.S it forms a crystal line compound CH2Cl2(H2S)2 23aq (Forcrand, A Ch [5] 28, 17)

TRIMETHYLENE CHLORIDE v $\omega\beta$ Dichloro propane

METHYLENE CHLORO BROMIDE CHLORO BROMO METHANE

Tri methylene chloro-bromide v Chloro BROMO PROPANE

TRIMETHYLENE CYANHYDRIN v Nutrile of γ Oxy-butyric acid

TRIMETHYLENE CYANIDE C₃H₄N₂ 2 e CH₄(CH₄CN)₂ Glutaromtrale (274°) (H), (286°) (Perkin, C J 55, 702), (203° at 100 mm), (142° at 10 mm) (Krafft a Noerdlinger, B 22, 817) SG $\frac{15}{15}$ 9952, $\frac{2}{3}$ 9894 M M 5 136 (P) Formed from trimethylene bromide and alco hohe KCy (Henry, Bl [2] 43, 618, C R 100, 742) Liquid, sol water, alcohol, and chloro form, insol ether and CS₂ Yields glutaric acid on saponification Sodium reduces it in alcoholic solution to pentamethylene diamine and piperidine

TRIMETHYLENE-DI ETHYL ALKINE ETHYL OXYPROPYL AMINE

METHYLENE-ETHYL AMINE C₃H,N te EtNCH₂ (208° 1 V) V D 2 Formed by the action of ethylamine on formic aldehyde (tri oxymethylene) (Kolotoff, Bl [2] 43, 112, J R 17, 231) Liquid, with unpleasant odour, sol cold water, but separates again on warming, v sol alcohol HCl splits it up into ethylamine and trioxymethylene (formic paraldehyde)—B'2H,PtCl₂ Yellow crystalline pp An isomeride (CH₂),N₂Et₄ of this base is described by Lermontoff (B. 7, 1252) as an oil formed by heating

ethylamine with alcoholic methylene iodide at 100°—(CH.). N. Et. H. PtCl. Amorphous

100°—(CH₂)₄N₄Et₄H₂PtCl₆ Amorphous Methylene tetre ethyl-diamine C₉H₂₂N₂ is CH₂(NEt₂)₂ Tetra ethyl-diamine C₉m₂N₂ is CH₂(NEt₂)₂ Tetra ethyl-di-amido methane (169° i V) 8 10 Formed by heating trioxy methylene (formic paraldehyde) with diethyl amine in sealed tubes at 100° (Kolotoff, Bl [2] 43, 112, Ehrenberg, J pr [2] 36, 118) Inquid with peppery odour, sl sol water, miscible with alcohol, ether, and CHCl₃ Split up by dilute acids, even by oxalic acid, into NHEt₂ and formic aldehyde Combines with CS₂, forming C₉H₂₂N₂OS₂

Tetra - methylene tetra - ethyl - tetramine $C_{12}H_{28}N_4$? e $CH_2 < NEt$ CH_2 NEt CH_2 NEt CH_2 NEt CH_2 Formed by heating methylene iodide with alcoholic ethylamine at 100° (Lermontoff, B 7, 1252) Liquid, yielding amorphous salts $-B''H_2PtCl_6$ sl sol water

METHYLENE - ETHYL PHTHALIMIDINE $C_{11}H_{11}NO$ & e $C_{e}H_{4}$ C_{CO} NEt Obtained by heating $C_{22}H_{24}N_{1}O_{5}$ which is produced by adding aqueous ethylamine to phthalyl acetic acid (Mertens, B 19, 2369) Colourless oil, smelling of fresh carrots Volatile with steam, v sol alcohol and ether

METHYLENE DI-ETHYL DISULPHIDE C₅H₁₂S₂ te CH₂(SEt)₂ Formac addehyde cthyl mercaptal Ethyl derivative of di thio formic orthaldehyde (178°-181°) SG ²⁰ 987 Formed from methylene chloride and NaSEt in alcoholic solution (Niederist, A 186, 391, Fromm, A 253, 155)

METHYLENE DI ETHYL DISULPHONE

C₃H_{1,2}S₁O₄ ie CH₁(SO₂Et)₂ [104°] Formed
by the action of KMnO₄ and H.SO₄ on CH₁(SEt)₄
(Fromm, A 253, 156, cf Baumann, B 1°,
2811) Needles, v sol water and alcohol, sl sol
ether Chlorine forms CCl₂(SO₂Et)₂ [99°] crys
tallising in needles, while bromine produces
CBr₂(SO₂Et)₂ [132°]

Di-methylene di-ethyl trisulphone (Et SO₂CH₂)₂SO₂ [149°] Formed by treating formic aldehyde with H₂S₁, dissolving the product in aqueous NaOH, shaking with EtBr, and oxidising the product with kMnO₄ (Baumann, B 23, 1875) Sparingly soluble colourless plates METHYLENE_FURFURANE TRIHYDRIDE

C₃H₃O 2 & CH₂ CH₂ C(OH₂) (111°) at 718 mm

Formed by the action of solid KOH on methyl bromo propyl ketone (Lipp, B 22, 1207) Mobile liquid, m sol water Yields a hydrazide When heated with 5 pc HClAq at 100° it yields aceto propyl alcohol (methyl oxypropyl ketone) Probably identical with trimethylenyl methyl ketone of Perkin, jun (B 17, 1440)

TRI-METHYLENE GLYCOL C.H. O. 1 C.CH. (CH.OH.) (214°) SG § 10625 (Z), $\frac{166}{10536}$ (F) CE (0°-10°) 00060 SV 84 (Zander, A 214, 178, Lossen, A 254, 59) One of the products of the fermentation of glycerin by schizomycetes (Freund, M 2, 636)

Formation —1 By saponifying its diacetyl derivative with baryta water (Reboul, A Ch [5] 14, 491) —2 By warming trimothylene bromide with moist Ag₂O (Beilstein a Wiegand, B 16,

1497) -8 By allowing CH₂(CH₂Br)₂ to stand for some time with a large excess of water (Niederist, M 3, 839) -4 By boiling trimethylene bromide with dilute aqueous K2CO, (Z)

Properties -Viscid liquid, with sweet taste,

miscible with water

Reactions —1 Fuming HClAq at 100° con verts it into CH₂(CH₂Cl)₂ •-2 Trimethylene glycol (35 g) heated with aldehyde (12 g) at 100° yields the ethylidene derivative (v infra)

Dracetyl derivative CH₂(CH₂OAc)₂ (210° cor) (c 111°) SG ² 991, ¹⁸ 1070 11 Formed by boiling CH₂(CH₂Br)₂ with NaOAc (Reboul)

Ethylidene derivative C₅H₁₀O₂ re CH₂CH₂O CH CH, V D 3 62 (calc 3 53) Obtained by heating the glycol with aldehyde at 100°, the yield being nearly the theoretical (Lochert, A Ch [6] 16, 49) Colourless liquid, with slight aldehydic odour Dissolves in 1; volumes of water, v sol alcohol and ether Separated from its aqueous solution by CaCl2 and by KOH Saponified by boiling water, al kalis, and dilute acids aldehyde and CH₂(CH Cl) With PCl, it yields

Amylidene derivative C,H14O2 1e CH CH O CH C₄H, (c 165°) S G 2 995 VD 503 (calc 498) Formed by heating tri methylene glycol (35g) with valeric aldehyde (20g) in a sealed tube at 125° Colourless mo bile liquid, v sl sol water, v sol alcohol and ether Saponified by boiling water

Heptylidene derivative C10H OO2 16 CH $\stackrel{\text{CH}_2 \text{ O}}{\text{CH}_2 \text{ O}}$ CH C₆H₁₃ (c 216°) 8 G $\stackrel{\text{Q}}{\text{O}}$ 933 From the glycol (30 g) and heptoic aldehyde (cenanthol) at 160° (L)

Bromhydrin v Bromo PROPYL ALCOHOL TRI METHYLENE IMINE C3H, N i e

CH, CH, NH (65°-80°) Formed, together with a polymeride C_aH_{1,}N (160°-167°), from CH_aBr CH₂ CH₂ NH₂ and NaOH in the cold (Gabriel a Weiner, B 21, 2669) Volatile liquid, smelling like NH, and fuming in the air Eagerly combines with CS₄ - B'HAuCl₄ -B' H.PtCl₆ -B'C₆H (NO),OH [167] METHYLENE IOI

IODIDE CH,I, Di rodo methane [4°] (152° at 330 mm) SG $\frac{15}{15}$ 3 2853, $\frac{25}{25}$ 3 2656 MM 18 827 at 15° (Perkin, C J 45, 464

Formation -1 By heating iodoform (4 mols) with NaOEt (9 mols) dissolved in alcohol (But lerow, A 107, 110, 111, 242, cf Bruning, A 104, 187) -2 By heating chloroform with HIAq at 130° (Bluducho, Z [2] 7, 91) -3 By heating 10doform (50 g) with cone HIAq (200 g) to boiling (127°) and adding phosphorus (Lieben, Z 1868, 712, Baeyer, B 5, 1095)—4 From methylene chloride and CaI, at 75° (Spindler, A 231, 262) -5 By warming a mixture of iodoform (5 pts), water (2 pts) and reduced iron (5 pts), and fractionally distilling in vacuo (Cazeneuve, C R 98, 369) -6 An alcoholic solution of 10do form is decomposed by light, yielding CH,I, and Oxalic acid accelerates the reaction (Mulder, R T C 7, 316)

Properties -Yellowish liquid, boiling with partial decomposition at 180°.

Reactions -1 Potassium has no action in the cold, but on heating it acts with explosive violence -2 Heated with copper and water, the products are cuprous iodide and a mixture of CO, methane, CO, and ethylene (Butlerow, A 120, 356) —3 Silver acetate forms the diacetyl derivative of formic orthaldehyde CH. (OAc), -4 Silver oxalate yields formic paraldehyde (trioxymethylene) -5 Chlorine yields CH₂Cl₂-6 Bromine forms CH2Br2 (Arnhold, A 240, 207) -7 Converted by PCl, at 70° into methylene chloride and a trace of chloriform (Höland, A 240, 227) —8 Alcoholic Na₂S yields thioformic aldehyde —9 NMe, combines with formation of (CH.I)NMe₃I -10 Annline forms CH₂(NHPh)₂ 11 Mercury forms IHg CH₂I (Sakurai, C J 37, 658)

Trimethylene iodide v Di 1000 PROPANE DI-TETRAMETHYLENE KETONE v DI-

TETRAMETHYLENYL KETONE METHYLENE-MALONIC ETHER $C_8H_{12}O_4\nu$ e CH C(CO₂Et)₂ [156°] Formed by heating malonic ether with methylene iodide and NaOEt (Zelinsky, B 22, 3294) Mobile liquid Isomeric with fumaric and maleic ethers. With bromine it yields CH₂Br CBr(CO₂Et)₂ (185°-190° at 75-85 mm)

Polymeride {CH₂ C(CO_.Et)₂}₂ [156°] Ac companies the preceding (Z) Minute amorphous granules, insol water, m sol ether and alcohol Its molecular weight determined by

Raoult's method is 342 (calc 344)

DI-METHYLENE-DI-METHYL-DIAMINE $C_1H_{10}N_2$ i.e. $(CH_2)_2N_2Me_2$ VD (H=1) 41.5 (calc 43) Formed by passing a mixture of tri methylamine and hydrogen through a red hot tube (Romeny, B 11, 835) Crystalline Hot dilute HClAq splits it up into formic aldehyde and methylamine -B"H PtCl,

A base, boiling at about 207°, formed by the action of methylamine upon trioxymethylene (formic paraldehyde) is perhaps identical with the preceding (Kolotoff, Bl [2] 45, 253)

TRIMETHYLENE - HEXA - METHYL - DI **AMINE** $(C_3H_6)N$ $(CH_3)_6$ Formed by heating trimethylene bromide (CH_6Br) with trimethyl Formed by heating

Salts - B'H2Br2 aq soluble colourless needles -B' H, Cl2PtCl, sparingly soluble (Roth, B 14, 1351)

METHYLENE METHYL BUTENYL DI KETONE CH, CO CH. CO C,H, Acetyl mesityl Acetyl angelicyl methane Formed as a secondary product in the prepara tion of methylene dimethyl diketone by the action of acetone and NaOEt on acetic ether (Claisen a Ehrhardt, B 22, 1012, Bl [3] 1, 498) soluble in aqueous alkalis Its alcoholic solu tion gives a red colour with FeCla Cuprio acetate in concentrated solutions gives a dark green pp -CuA' [123°] Crystalline, v sol warm alcohol and ether

METHYLENE DIMETHYL ETHER v D.

methyl ether of Ortho Formic aldehyde METHYLENE METHYL ETHYL DIKE TÔNE CoH10O2 1 e C2H5 CO CH2 CO CH3 CO CH, Acetyl S G 15 9538 promonyl methane (158°) Formed by the action of EtOAc and NaOAc upon methyl ethyl ketone (Classen a Ehrhardt, 22, 1014) —Cu(C₆H₈O₂)₂ [179°] Slender blue needles (from hot alcohol) METHYLENE METHYL HEXYL DIKE FONE $C_{10}H_{18}O_2*.e$ CH_1 CO CH_2 CO C_6H_{11} (229°). Formed from methyl hexyl ketone, AcOEt, and AcONa (Claisen a Ehrhardt, B=22, 1015) aquid $-Cu(C_{10}H_{11},O_2)_2$ [122°] Crystalline METHYLENE DI-METHYL DIKETONE

 J₆H₈O₂ re OH₂(CO CH₃), Dr acetyl methane
 dcetyl-acetone (186°) S G 15 987 (Combes)
 Preparation —1 By slowly adding acetone 1 mol) to a mixture of acetic ether (3 mols) ind dry NaOEt (1 mol) heated on the water The product is poured into ice cold vater, and the aqueous liquid mixed with HOAc. and cupric acetate, which ppts Cu(C,H,O2), The yield is 35 pc of the weight of acetone imployed (Claisen, Bl [3] 1, 498) -2 Acetone 58 pts) mixed with EtOAc (33 pts) is treated n the cold with sodium wire (2 3 pts) nost of the sodium is dissolved, the mixture is neated on a water bath The product is ppd as supric salt, the yield of ketone being 55 p c of he acetone employed (Classen a Ehrhardt, B 22, 1009) In either case the diketone is ob ained from the copper compound by adding lilute H2SO, and extracting with ether -3 From he compound C₁₂H₁₀O_cAl₂Cl₆ (obtained from icetyl chloride and AlCl₂) by adding water and attracting with chloroform The yield is 85 p c

of the theoretical (Combes, A. Ch. [6] 12, 211)
Properties—Colourless liquid with pleasant icetic odour, sol water, v. sol aqueous HCl, miscible with alcohol, ether, and chloroform

Not attacked by PCl₃

Phenyl hydrazıne Reactions -1 forms phenyl dimethyl pyrazole $CMe \stackrel{CH}{\leqslant_{NPh}} OMe$ 270 5°) (Combes, Bl [2] 50, 145) -2 Potash lecomposes it into acetone and KOAc -3 PCl, yields HCl and C₅H₆Cl₂ (145°), a di chloro amyl one which readily combines with bromine 1 Sodium amalgam yields isopropyl alcohol and ofnacone But in acid solution the products of eduction by sodium amalgam are di oxy pentane CH₂ CH(OH) CH₂ CH(OH) CH₃, and a tetra nydric alcohol analogous to pinacone —5 Conc HIAq at 185° reduces it to pure n pentane (38°) At lower temperatures it forms CH2(CHI CH3) and CH, CHI CH, CH, CH, -6 Excess of thlorine in sunlight yields (CCl₃ CO)₂CH₂ as final product -7 Bromine attacks the diketone finally producing (CBr, CO)2CH2 ngorously, 108°] —8 Oxidation by CrO, or by KMnO yields acetic acid -9 Warm dilute nitric acid produces CH₂(NO₂)₂ and HOAc —10 Dry am nonia passed into its ethereal solution ppts white pearly scales of the ammonium salt CH(NH₄)(CO CH₃)₂—11 Ethylene dramme (2 mols) forms C₂H₄(N CMe CH₂Ac)₂ [111°] which yields a violet cupric salt $C_{12}H_{18}N_2O_2Cu$ [137°] and a hydrochloride $C_{12}H_{20}N_2O_2H_2Cl_2$ melting above 280° Other diamines act in like manner (Combes, C R 108, 1252) -12 Unites with benzidine (1 mol) forming a base melting at 195° (Combes) -13 Aldehyde ammonia (mol) ht 100° forms diacetyl tri methyl-pyrdine diahydride O₁₂H₁₇NO₂ [153°] (Combes, Bl [3] 1, 14).

14 Tolylene m diamine at 100°, followed by H₂SO₄, yields amido trimethyl quinoline C₁₂H₁₄N₂ [191°] (Combes, C R 108, 1254) -15 SO₂Cl₂ forms the chloro derivative C₅H₇ClO₂ (156°) (Combes, C R 111, 272)

Salts —CH(NH_a)(CO CH_a)_a. Pearly scales, ppd by passing NH_a into the ethereal solution Decomposes readily into acetone and acetamide. -Ac₂CHNa Formed by dissolving sodium in the diketone (Combes, C R 104, 920) White sixsided prisms, insol ether Decomposed by water into acetone and NaOAc With ethyl iodide at 140° it gives CHEt(CO CH₂), a liquid boiling at 171° Amyl iodide, in like manner, yields C₅H₁₁ CH(CO CH₂). The second atom of hydrogen in the methylars group may in sind company. gen in the methylene group may, in such com pounds, be displaced by Na, and by acting with an alkyl iodide R'I upon RONa(CO CH₃), we may obtain compounds of the form RCR'(CO CH₃), These reactions take place with hardly any These homologues secondary decompositions of methylene. dimethyl diketone are decom posed by potash like the diketone itself (Combes, A Ch [6] 12, 211) ClCO₂Et acting on the sodium derivative of methylene dimethyl diketone forms C(COMe)₂(CO.Et)₂ (Classen a Zedel, B 21, 3397)—KCHAc₂ White six sided prisms, sl sol alcohol, insol ether Formed by adding KOEt to an alcoholic solution of the diketone Decomposed by hot water into acetone and KOAc -Mg(CHAc₂)₂ (dried at 125°) From the diketone and magnesium carbonate (Combes, C R 105, 868) Transparent six sided prisms -Al(CHAc₂)₃ A by product in the rectification of the diketone, from which it may be obtained by treatment with AlCl_s Small red crystals, insol water, sl sol alcohol, v sl sol ether Can be partially volatilised Acts on polarised light Not decomposed by alcoholic NH₃ —Cu(HCAc₂)₂ (dried at 125°) Pale blue needles, obtained by adding cupric acetate or chloride to an aqueous solution of the diketone Insol water, the ppn being complete in dilute solutions At 65° it forms with COCl₂ dissolved in benzene a crys talline compound melting at 121° (Thomas a Lefèvre, Bi [2] 50, 193) —Fe(HCAc2), Red crystals, deposited from the ethereal extract of the red solution obtained by adding FeCl, to the diketone dissolved in water -Pb(HCAc) From the diketone and lead carbonate Transparent crystals, sol water

Oxim CH, CO CH, C(NOH) CH, Anhy dride CH CMe N (142°) 8 G 1 985

Formed by the action of hydroxylamine on the diketone (Zedel, B 21, 2178) Colourless oil, with peculiar alkaloidal odour

Dioxim CH₂(C(NOH) CH₃)₂ [150°] Large

transparent crystals (from ether)

Phenyl methyl hydraside CH₂ CO CH₂ C(N₂PhMe) CH₃ (Kohlrausch, A 253, 22)

Di-methylene di-methyl triketone (CH₂ CO CH₂)₂CO Di-acetyl acetone [49°]
Formed from its anhydride (v infra) Plates
Sl sol water, sol alkalis, warm alcohol, and ether FeCl₂ gives a deep-red colour Converted by NH₂ into oxy-di methyl pyridine [225°]

by NH, into oxy-di methyl pyridine [225°]

Anhydride COCCH CMeOD Di methyl pyrone [182°] (249°) Formed by the action of HIAq on dehydracetic acid at a high temperature (Feist, B 22, 1570, A 257, 253) The yield is 70 pc of the theoretical Crystals, ve sol water Converted by baryta, followed by HCl, into di methylened i methyl tri ketone The carboxylic

acid of this anhydride is dehydracetic acid. The petroleum ether dicarboxylic ether $CO < C(CO_2Et) CMe > O [80^\circ]$ 8 8 at 20° is formed by the action of COCl2 on copper acetoacetic ether, and is converted by P_2S_4 into $CS < \frac{C(CO,Et)}{C(CO_2Et)} \frac{CMe}{CMe} > O$ [110°] (Conrad, B 19, 22, 20, 152, 2111)

Di phenyl hydrazide (CH₃ C(N HPh) CH₂),CO [142°]

Trimethylene methyl ketone v TRIMETHYL ENYL METHYL KETONE.

Tetramethylene methyl ketone v Tetra MFTHYLI NYL METHYL KETONE

METHYLENE DIMETHYL ETHER

Methul ether of formic orthaldehyde

METHYLENE DIMETHYL DIOXIDE Methyl ether of Formic orthaldehyde, vol 11 p 570

METHYLENE METHYL PHENYL DI KETONE v BFNZOYL ACETONE

METHYLENE METHYL-PHTHALIMIDINE C=CH₂ C₁₀H₉ON ie C_eH₄ NMe Formed by heat

ing phthal methyl imidyl-acetic acid

crystals V sol alcohol, Volatile with steam ether, and chloroform, more spanngly sol Very unstable body (Gabriel, B 18, 2454)

METHYLENE METHYL PROPYL **KETONE** $C_7H_{12}O_5$, i.e. CH_3 CO CH. CO C_3H_7 (175°) S G $\frac{15}{2}$ 9411 Formed by the action of EtOAc and NaOAc upon methyl propyl ketone (Claisen a Ehrhardt, B 22, 1015) Formed also from butyiic ether, acetone, and NaOEt Colourless oil Boiling alkalis yield acetic and Yields C₆H₅N, CHAc COPr [55°] butyric acids crystallising in yellow prisms -Cu(C,H11O2)2 [161°] Blue needles

TETRA METHYL TRIMETHYLENE DI-PYRROLE C₁₅H ₂N₂z e (| CH CMe CH CMe on ch,),ch,

[77°] Formed by heating acetonyl acetone with alcoholic tri methylene diamine at 120° (Paal a Schneider, B 19, 3157) Crystalline

METHYLENE DI METHYL DISULPHONE (CH, SO), CH₂ [141°] Formed from methyl mercaptan and methylene chloride, and oxida tion of the product (Baumann, B 23, 1875) On treatment with bromine water it Plates gives CBr₂(SO₂Me)₂ [234°]

Dı methylene di methyl trısulphone (CH, SO, CH,), SO, [185°] Formed by satu rating a solution of formic aldehyde with H,S, extracting with ether, evaporating, dissolving the residual oil in aqueous NaOH, adding MeI, and oxidising with KMnO4 (Baumann, B 23, 1872) Prisms, v sl sol cold water, alcohol, and ether Yields with bromine-water insoluble C4H6Br4S3O6 [190°]

TRIMETHYLENE TRINITROSAMINE

C₃H₆N₆O₃ : e (CH₂N NO)₃ [106°] Formed by the action of nitrous acid upon hexamethyleneamine (F Mayer, B 21, 2883) Yellow needles or prisms (from alcohol), v. sol. alcohol, insol.

Decomposed by water with production of formic aldehyde

METHYLENE DI-OCTYL OXIDE v Octul ether of Formic orthaldehyde

METHYLENE OXIDE 18 FORMIC ALDEBYDE

METHYLENE-DI-OXY compounds v Methyl

ene derivatives of DI OXY compounds METHYLENE DI PHENYL DIAMINE

DI PHENYL METHYLENE DIAMINE

METHYLENE DI PHENYLENE Dι PHENYLENE METHANE

METHYLENE DIPHENYLENE OXIDE v DI PHENYLENE METHANE OXIDE

METHYLENE DIPHENYL DIKETONE v DI PHENYL METHYLENE DIKETONE

TRIMETHYLENE PHENYL KETONE v PHENYL TRIMETHYLENE KETONE

Tetramethylene phenyl ketone v Anhydride of Phenyl oxybutyl ketone

METHYLENE DIPHENYL OXIDE v Di

PHENYLENE METHANE OXIDE METHYLENE HEXAPHENYL

PHONIUM IODIDE v Methyleno di iodide of TRI-PHENYL PHOSPHINE

TRIMETHYLENE DI PHTHALAMIC ACID C₁₀H₁₀N₂O₆ is CH₂(CH₂NH CO C₆H₄ CO H), [70°-123°] Obtained by boiling trimethylene dı phthalimide with potash (Gabriel, B 21, 2670) Crystalline Decomposed by water On boiling with aqueous HCl it is converted into phthalic acid and trimethylene-diamine

METHYLENE PHTHALIDE C,H,O, 1.4. C=CH2 C_4H_4 Anhydride of o Oxy vinyl-

>0

\c=0 [60°] Formed by heating benzow acid phthalyl acetic acid in vacuo (Gabriel, B 17, 2521) Small glistening crystals Soluble in hot water, easily in alcohol, ether, benzene, &c Volatile with steam It readily polymerises Combines with Br (1 mol)

glistening crystals Formed by the combination of methylene phthalide with bromine warming with aqueous KOH it yields aceto phenone o carboxylic acid C₆H₁(CO₂H) CO CH₂ Boiled with water it gives methylene phthalide oxide C₂H_eO₃ (Gabriel, B 17, 2524)

Methylene-phthalide oxide C,H,O, [146° Long needles Formed by boiling the dibromide of methylene phthalide with water Formed also by the action of water on the product of the bromination of acetophenone o carboxylic acid (Gabriel, B 17, 2524)

Di chloro-methylene phthalide C.H.Cl.O. t s.

$$C_0H_4$$
 $\begin{array}{c} C=CCl_2 \\ > O \\ C=O \end{array}$ [128°] Formed by passing

chlorine into a mixture of a chloro phenylacetic acid (1 pt) and HOAc (10 pts) Formed also by warming di chloro acetophenone carboxylic acid with conc H₂SO₄ (Zincke a Cooksey, A 255, 383) Long slender needles, gradually becoming compact when left in the liquid The needles are v sol hot alcohol, benz ene, HOAc, and benzoline, the compact crystals are soluble with difficulty Alcoholic potash

converts it into di chloro acetophenone ocarboxylic acid Forms a dichloride CCI_CCI3

00 which crystallises in colourless prisms [94°], v sol alcohol and HOAc, and tonverted by alcoholic potash into phthalic

Bromo methylene phthalide v vol 1 p 580

Isomeride of methylene phthalide v Метн YLFNE PHTHALYL

Polymeride of methylene phthalide $C_{18}H_{12}O_4$ [216°] Obtained by allowing a solu tion of acetophenone carboxylic acid (1 pt) in H,SO, (2 pts) to stand in the cold, and then ppg with water (Roser, B 17, 2620, Gabriel, B 17, 2666, cf Acetophenone o carboxylic acid, reaction 2) Plates Insol water and cold alkalis, sl sol alcohol, v sol HOAc

 $Oxim C_{18}H_{19}NO_{4} [180^{\circ}]$ Obtained by heating the substance with alcoholic hydroxylamine hydrochloride at 160° Crystalline granules (from dilute HOAc)

METHYLENE-DI-PHTHALIMIDE

 $\mathrm{CH_2(N < }^{\mathrm{CO}}_{\mathrm{CO}} > \mathrm{C_6H_4)_2}$ [226°] Formed by heat ing potassium phthalimide (2 mols) with methylene 10dide (1 mol) at 175° (Neumann, B 23, 1002) Light brown crystals (from HOAc), insol dilute alkalis Yields phthalic acid on heating with HClAq

TRIMETHYLENE-DI-PHTHALIMIDE

C₁₉H₁₄N₂O₄ 1 e C₈H₄O₂ N CH₂ CH. CH₂ N C₈H₄O₂ [198°] Formed by the action of tri methylene bromide on potassium phthalimide (Gabriel, B 21, 2669) White needles, m sol hot HOAc, sl sol ether, CS2, chloroform, and cold alcohol, v sl sol water and petroleum ether Converted by heating with KOH into tri methylene di Converted phthalamic acid C3H6(NHCOC6H4CO2H)2 composed by heating with HCl at 180° into phthalic acid and tri methylene diamine

METHYLENE-PHTHALYL C.H.O. ...

 $C_8H_4 < CO > CH_2$? [219°] Fine yellow needles

Formed, together with o tribenzoylene benzene, by heating phthalic anhydride with malonic ether and sodium acetate (Gabriel, B 14, 925)

METHYLENE-DI-PIPERIDINE

 (230°) CH2(NC3H10)2 Formed by distilling piperidine with trimethylene oxide (formic par aldehyde) (Ehrenberg, J pr [2] 36, 126) Liquid, with pepper like smell Is decomposed by dilute acids into its constituents CS2 forms an addition product B"CS₂, [58°], sol alcohol and ether, insol water

METHYLENE-TETRA-PROPYL-DIAMINE CH₂(NPr₂)₂ (220°) Formed by distilling di-propylamine with trimethylene oxide (formic paraldehyde) (Ehrenberg, J pr [2] 36, 122) Inquid, sl sol water, v sol alcohol, ether, and chloroform

METHYLENE DI-PROPYL OXIDE # Dipropyl ether of Formic orthaldehyde

TRI-METHYLENE SELENO-UREA v Sele-MIUM COMPOUNDS, ORGANIC

METHYLENE SULPHIDE C. THIOTORMIC ALDEHYDE.

Tri methylene tetrasulphide C.H.S. te. CH₂ \langle CH₂ S CH₂ S \rangle [84°] Formed by the action of H2S on formic aldehyde (Baumann, B 23, Colourless needles, msol water, m sol alcohol and ether, v e sol CHCl, and benzene **METHYLENE SULPHOCYANIDE** C,H,S,N,

ie CH₂(SCy)₂ [102°] Formed by digesting potassium sulphocyanide (2 mols) with methyl ene iodide (1 mol.) in alcoholic solution for 2 or 3 hours on the water bath, ppg with water, and recrystallising from alcohol (Lermontoff, B 7, Crystals, v sol alcohol and ether, m 1282) sol hot, nearly insol cold, water Oxidised by cone HNO, to methane disulphonic acid

TRI-METHYLENE-TRISULPHONE

C₃H₆S₃O₆ ie CH₂ SO₂ CH₂ SO₂ Formed by oxidising thioformic paraldehyde (trithio form aldehyde) with KMnO, (E Baumanna R Camps, B 23, 69) Crystalline powder, insol water, dilute acids, alcohol, ether, chloroform, and glacial acetic acid, v sol cold caustic soda, ammonia (by warming), and sodic carbonate Expels CO from Na CO₃ on warming Conc HNO₃ and H₂SO₄ have no action even on warm Its solution in HSO, is ppd by water unaltered It partially sublimes The six hy drogen atoms can be displaced by alkyl groups The hexamethyl derivative

 $CMe_2 < SO CMe_2 > SO_2$

is identical with the product obtained by B Jaffé, E Baumann, and Fromm (B 22, 2598, 2609) by oxidising trithio acetone

TRIMETHYLENE-DI-SULPHONIC ACID so called v Propane di sulphonic acid

METHYLENE TRI-THIO-CARBONATE

CH₂<S>CS Separates on gently heating CS(SNa)2 with methylene iodide in alcoholic solution (Husemann, A 126, 292) Amorphous yellowish white powder, insol water verted by fuming nitric acid into methane di sulphonic acid

TRIMETHYLENE THIO UREA C,H,N S i e CH CH, NH CS [198°] Formed, together with ammonium sulphocyanide, by heating the sulphocyanide of trimethylene diamine C,H₆(NH₂),(HNCS), (Lellmann a Wurthner, A 228, 232) White needles (from chloroform mixed with light petroleum) Sol water, alco hol, CHCl,, and benzene, m sol aqueous NaOH, $\begin{array}{ll} \text{nnsol light petroleum} & \text{Forms a sparingly soluble} \\ \text{compound with } \text{HgCl}_{2} \end{array}$

Trimethylene-\(\psi\) thio-urea

CH₂ CH₂ S NH Formed by evaporating a solution of γ bromo propyl amine hydrobromide and potassium sulphocyanide to dryness at 100° (Gabriel a Lauer, B 23, 94) Liquid, v sol water forming an alkaline solution, from which it can be extracted by benzene —B'HBr [136°]
—B'C_eH₂(NO₂)₃OH [128°] Long needles
TRIMETHYLENE-UREA C₄H₈N₂O 2 e

OH₂ CH₂ NH CO Oxy-pyrimidine tetrahy dride [260°] Formed by heating trimethylene diamine (1 mol) with carbonic ether (1 mol) for 6 hours at 180° (Fischer a Koch, A 282, 224). White needles, v sol water, sl sol alcohol and ether Its solution is neutral, and is not ppd by HNO₃ or oxalic acid By chromic acid mixture it is oxidised to a compound C4H4N2O2 crystallising in plates [275°]

Trimethylene ψ-urea CH₂ CH₂ NH CNH

or $CH_2 < \stackrel{CH}{CH_2} \stackrel{O}{N} > C$ NH. Formed by evaporating a solution of equivalent qualitities of potassium cyanate and γ bromo propyl amine hydrobromide (Gabriel a Lauer, B 23, 95) Thick liquid, v sol water —B'C₂H₂(NO₂),OH [200°] Long yellow needles

Trimethylene-di-ures CH₁₂N₁O₂ ie CH₂(CH₂NH CO NH₂)₂ [182°] Formed by warming a dilute aqueous solution of tri methylene diamine hydrochloride with silver cyanate (F a K) White needles, v sol water,

sl sol alcohol, insol ether
METHYLENE VIOLET C1.H12N2SO 16.

diphenylene sulphide Oxy dimethylamido thio diphenylimide Formed by boiling a solution of methylene blue (base) Formed also by oxi dising a mixture of di methyl di amido phenyl, mercaptan, and phenol (Bernthsen, A 230, 171, 251, 96) Needles, v sl sol water, sl sol alco hol, ether acetone, chloroform, benzene, ligroin, and cumene, with a reddish brown fluorescence, v sol aniline, without fluorescence -B'HCl sl sol cold dilute HClAq

METHYLENITAN ι vol 11 p 571 DI METHYL ENNYLENE DIKETONE

C13H24O2 1 c CH (CH2 CHEt CO CH3) (208° at 110 mm) acityl di ethyl n pentane Formed from its dicarboxylic ether by treatment with alcoholic potash (Kipping a Perkin, jun, C J 57, 33) Colourless oil, with slight aro matic odour, v sl sol water, miscible with alcohol and ether It dissolves without change in conc H SO, forming a yellowish brown solu tion It does not combine with NaHSO,

Orim CH (CH, CHEt CMe NOH), Obtained by heating the ketone with an alcoholic solution of hydroxylamine, evaporating, adding water, and extracting with ether Minute colour less crystals (from benzene ligroin), v sol al cohol, ether, HOAc, benzene, and aqueous alkalıs

DI-METHYL ENNYLENE DIKETONE DI-CARBOXYLIC ETHER

CH₂(CH₂CEt(CO CH₂) CO₂Et)₂ as Di acetyl as di ethyl pimelic ether [45°] Obtained, to gether with compounds of low boiling point, when sodium ethyl acetoacetic ether is heated with an alcoholic solution of trimethylene bromide on a water bath (Kipping a Perkin, jun, C J 57, 81) Very slender needles (from ether alcohol), v sol ether and alcohol, v e sol benzene, light petroleum, xylene, and chloro form, insol cold water Gives no colour with Readily decomposed by warm alcoholic potash

METHYL ENNYL RETONE CH. CO C.H. (16°) (224°) S G 17 5 8295 The chief constituent of oil of rue, obtained by distilling Ruta | Perkin, jun, C J. 51, 285)

graveolens with steam (Greville Williams, T 1858 [1] 99, Hallwachs, A 113, 109, Harbordt, A 123, 293, Giesecke, Z [2] 6, 429, cf Gerhardt C R 26, 225, 361, Cahours, C R 26, 262) Occurs in the essential oil obtained from lime leaves (citrus Limetta) (F Watts, C J 49, 316) Formed also by distilling a mixture of calcium acetate and calcium decoate (Gorup Besanez a Grimm, A 157, 275, B 3, 518), and by boiling octyl acetoacetic ether with alcoholic potash (Guthzeit, A 204, 4) It is oxidised by chromic acid mixture to acetic and ennoic acids Sodium amalgam reduces it, in alcoholic solution, to sec hendecyl alcohol (229°), SG
22 826 It combines with NH, With alka 12 826 It combines with NH₃ line bisulphites it forms compounds such as $C_9H_{19}CMe(OH)SO_3NH_4$ aq, which crystallises in pearly plates PCl₃ converts the ketone into C₁₁H₂₂Cl₂, which is resolved by distillation into HCl and C₁₁H₂₁Cl (222°) Oxim C₂H₁₂ CMe NOH

[42°] prisms (from alcohol), v sol ether (Spiegler, M

5, 242, B 17, 1575) METHYL ENNYL KETONE CARBOXYLIC ACID CH₃ CO CHEt CH₂ CH₂ CH₂ CHEt CO₂H « Acetyl-a∈ di ethyl-caproic acid Formed, together with di methyl ennylene diketone and acetic acid, by boiling di ethyl ennylene diketone dicarboxylic acid with alcoholic potash (Kipping a Perkin, C J 57, 36) Thick oil, miscible with alcohol, ether, and benzene -AgA' Amorphous pp, m sol hot

Oxem CH, C(NOH) C,H, CO,H Minute plates (from benzene ligroin), v sol alcohol and benzene, sl sol ligroin, sol alkalis and conc HClAq

TETRAMETHYLENYL-CARBINYL-AMINE

C3H11N re CH2 CH CH2NH2 (83°) methylenylamine' Formed from the nitrile of tetramethylene carboxylic acid CH₂CH₂CH CN by reduction in alcoholic solution with sodium (Freund a Gudeman, B 21, 2692) Oil, with alkaline reaction, which absorbs CO₂ from the air -B'HCl Crystallises from alcohol ether, v sol water and

alcohol, insol ether —B',H,PtCl, Crystalline TETRAMETHYLENYLCARBINYL - THIO -UREA CoH12N2S 2 6

CH, CH₂ CH CH, NH CS NH, [68°] pared by the action of ammonium sulphocyanide upon the hydrochloride of tetramethylenylcarbinyl amine (Freund, B 21, 2697) needles (from water or alcohol)

TETRAMETHYLENYLCARBINYL UREA C₆H₁₂N₂O to CH₂CH₂CH CH₂NH CO NH₂ [116°] Obtained by evaporating a solution of tetramethylenylcarbinylaminehydrochloride with potassium cyanate (Freund, B 21, 2697) Needles, sol alcohol, v sol hot, m sol cold

DI-TETRAMETHYLENYL KETONE C.H.O $\bullet e \quad CH_2 < \stackrel{CH_2}{CH_2} > CH \quad CO \quad CH < \stackrel{CH_2}{CH_4} > CH_2 \quad (205^\circ)$ A product of the distillation of calcium tetra methylene carboxylate with lime (Colman a. Oil, smelling of peppermint, combines with NaHSO, Bromine reacts, giving off HBr

Oxim [51°

TRIMETHÝLENYL METHYL KETONE

CH CO CH, or

CH₂ OH CH₂ CH₂ CH₂ Acetyl - trimethylene Methylene furfurane tetrahydride (114°) SG 15 9047, 25 8971 MM 5 245 at 22 3° Formed by distilling its carboxylic acid (Perkin, jun, C J 47, 836, 51, 832, B 17, 1440) The same substance appears to be formed by treating methyl bromo propyl ketone with solid potash (Lipp, B22, 1207) Oil SI sol aqueous NaHSO₃ Gives an oily phenyl-hydrazide Does not combine with water when left in contact with it in the cold According to Lipp the formula may be written CH₂ C CH₂ CH₂ since it yields methyl oxy propyl ketone (acetopropyl alcohol) on heating with dilute HClAq at 100°

Tetramethylenyl methyl ketone CeH10O 1 e OH₂ CH₂ CH CO CH₃ or CH₂ CH CMe OCH₂ CH₂ CH₂ CH CMe

or CH₂ CCC_{O-CH₂}CH₂ CH₂ Anhydride of methyl oxy butyl ketone Anhydride of acetobutyl al **c**ohol Acetyl tetramethylene (137°) A product of the distillation of calcium tetramethylene carboxylate with lime (Colman a Perkin, jun C J 51, 237, B 16, 1789, 19, 3112) Formed also by heating acetobutyl alcohol (Perkin, B 19, 2558) Oil, smelling of peppermint, combines with NaHSO, forming a crystalline body, v sol water

TRIMETHYLENYL METHYL KETONE CARBOXYLIC ACID C.H.O. 1 e

<CH₂>C(CO₂H) CO CH₃ or

OH₂ CCH(CO₂H) CH, Methylene furfurane tetrahydride carboxylic acid Obtained by sa ponifying its ether which is formed by the action of ethylene bromide and NaOEt on aceto acetic ether (Perkin, jun, B 16, 2136, 19, 2561, C J51, 823, Lipp, B 22, 1210) Thick oil, converted by boiling with water into CO2 and acetyl propyl alcohol CH₃ CO CH, CH, CH₂OH (145° at 100 mm) — AgA' Easily soluble crystalline nodules Ethyl ether EtA' (196°) S G 15/15 1 0517, 25/5 1 0439 MM 8 198 at 15° According to

Perkin, the physical constants of this ether indi cate the presence of the trimethylene ring Con verted by HBr into brome ethyl acete acetic ether CH, CO CH(CH₂ CH₂Br) CO₂Et Phos phorus pentachloride, followed by water, forms an oil $C_8H_{,2}O_2Cl_2$ (173° at 150 mm), which may possibly be chloro ethyl chloro-crotonic ether CH₂ CCl C(CH₂Cl CH₃) CO₂Et, since it is reduced by sodium amalgam to di ethyl acetic ether, and by zinc dust and HCl to CH₂ CCl CEt CO₂H

Phenyl hydraside of the ethyl ether

C₁₄H₁₈N₂O₂ Amorphous solid Trimethylenyl methyl ketone dicarboxylic acid $C_7H_8O_8$ 2 $e < \stackrel{CH_2}{CH_2} > C(CO_2H)$ CQ CH_2 CO_2H , or CO,H CH C CH(CO,H) CH, Methylene-

furfurane tetrahydride dicarboxylic acid 175°] Obtained from the ether which is got by acting on sodium acetone dicarboxylic ether with ethylene bromide (Perkin, C J 51, 847) White crystalline solid, sl sol water and chloroform, v sol other solvents Boiling water splits it up into CO2 and acetyl propyl alcohol -- Ag2A"

Tetramethylenyl methyl ketone carboxylic acid $C_7H_{10}O_3$ te $OH_2 < CH_2 > C(OO_2H)$ CO CH_3 [115°] The ether of the acid to which this con stitution was at first assigned by Perkin, jun (B 16, 208, 1787), was subsequently shown by him (B 19, 1244) to be indifferent towards phenyl hydrazine, and to possess a magnetic rotation at variance with this formula, and to behave rather as $CH_2 < \stackrel{CH_2}{O} - \stackrel{CH_2}{CMe} > 0$ CO_2Et The acid is a crystalline solid, obtained by saponifying its ether, which is formed by the action of tri methylene bromide and NaOEt on acetoacetic ether On boiling with water it is converted into acetobutyl alcohol with evolution of CO2 (Perkin, jun, B 19, 2557) On distillation it is split up into CO, and C,H10O

Salt -AgA' Ethyl ether EtA' (224°) VD 621 M M 10 195 Does not react with phenyl hydrazine Concentrated hydrobromic acid in the cold yields methyl ω bromo butyl-ketone CH, CO CH, CH, CH, CH, Br

METHYL ETHÂNE v PROPANE Di methyl-ethane v Butane Tri-methyl ethane v Pentane Tetra-methyl-ethane v HEXANE Penta-methyl ethane v HEPTANE Hexa-methyl-ethane v OCTANE

METHYL - ETHENYL TRICARBOXYLIC ACID v PROPANE TRICARBOXYLIC ACID

D1 methyl - ethenyl - tricarboxylic acid v BUTANE TRICARBOXYLIC ACID

METHYL ETHENYL ETHYL DIKETONE C₇H₁₂O₂ ie CH₃ CO CHMe CO Et (167°-170°) Formed by the action of NaOEt on a mixture of acetic ether and di ethyl ketone (Claisen a Ehr hardt, B 22, 1016) Colourless oils - CuA' Formed from the acid and Crystalline an ammoniacal solution of cupie oxide

METHYL ETHENYL TOLYLENE DIAMINE $\begin{bmatrix} 4 & 1 \\ 2 \end{bmatrix}$ CH₂ C₆H $\begin{pmatrix} NMe \\ N \end{pmatrix}$ CMe $C_{10}H_{12}N_2$ ıе [192°] Formed by reducing the acetyl deriva tive of nitro methyl p toluidine with tin and HCl (Niementovsky, B 20, 1878) Cubes (by subli mation at 110°), plates, or needles, v e sol alcohol, ether, and boiling water Its aqueous solution is coloured red by FeCl, The solution in alcoholic ammonia exhibits blue fluores cence —B'HCl ½aq Needles, v sol water — Tables, decomposed on B',H₂PtCl₅ [244°] Tables, decomposed on fusion—B'HI Formed by heating ethenyl tolyl ene diamine with MeI and MeOH at 130° (Nie

mentovsky, B 20, 1886) Grey plates
Methylo rodrdes B'MeI [221°] B'MeI, and NaOH Needles, v sol boiling alco hol and water, v sl sol boiling chloroform, insol ether—B'MeI, Formed in small quan tity in the preparation of B'HI as described above Black crystals

Methylo-hydroxide B'MeOH Formed by heating the methylo-rodide with KOH on the water bath White plates, sol boiling water, v sl sol cold water, v e sol alcohol and ether Forms the salts —*B'MeCl crystallising in rhombohedra, v e sol water—
*B'₂Me₂PtCl_e—Picrate [112°] crystallising in needles, m sol boiling water and alcohol

METHYL ETHER v DI METHYL OXIDE PENTA METHYL ETHOL A name some times employed to denote the alcohol CMe3 CMe2OH v HFPTYL ALCOHOL

METHYL ETHYL ACETAL v ALDEHYDE METHYL ETHYL ACETIC ACID v VALEBIC

Di methyl ethyl acetic acid v Hexoic acid METHYL ETHYL ACETOACETIC v ACETOACETIC ACID

METHYL ETHYL ACETOXIM v. Oxim of METHYL ETHYL KFTONF

METHYL ETHYL ACETOXIMIC ACID v

METHYL ETHYL ACETYLENE v PENTIN

METHYL ETHYL ACROLEÏN v HFXFNOIC ALDFHYDE

METHYL ETHYL ACRYLIC ACID v HEX ENOIC ACID

PENTA METHYL ETHYL ALCOHOL Tert HEPTYL ALCOHOL

DI METHYL ETHYL ALKINE Dr METHYL OXY ETHYL AMINE

METHYL ETHYL-ALLYL ALCOHOL

HEXFNII ALCOHOL

METHYL DI-ETHYL AMINE C.H., N MeNLt, Formed by distilling its methylo chloride, or by distilling triethylamine methylo hydroxide NEt, Me(OH) (V Meyer a Lecco, A 180, 184, Lossen, A 181, 379)—B'.H.PtCl. Monoclinic crystals (Hjortdahl, J 1892, 476)

MethylochlorideCeH16NClie Me2NEt2Cl Di methyl di ethyl ammonium chloride tained from the crystalline iodide Me,NEt,I, which is formed by heating dimethylamine with Etl or diethylamine with MeI (Petersen, A 91, 122, V Meyer a Lecco, A 180, 177) — (Me,NEt,Cl),PtCl, yellowish dimetric prisms, m sol water, sl sol alcohol and ether S 1 025 at 15° — (Me, NEt, Cl), HgCl, trimetric crystals (Topsoe, J 1883, 620) — Me, NEt, ClHgCl, — Me₂NEt₂Cl2HgCl₂ trimetric crystals — Me₂NEt₂ClAuCl₃ dimetric crystals

Methylo picrate [287°] Needles (Lossen, A 181, 374)

Ethylo hydroxide v Tri ETHYLAMINE

methylo hydroxide, vol 11 p 476 Di methyl ethyl amine NMe₂Et

product of the action of heat on trimethylamine ethylochloride (Collie a Schryver, C J 57, 770) Formed also by distilling NMe, Et OH

METHYL ŤRI ETHYĽ AMMONIUM COM POUNDS v Methylo hydroxide of Tri ethyl-AMINE

Di methyl di ethyl ammonium compounds e Methylo chloride of METHYL de ETHYL AMINE

Tri methyl-ethyl ammonium compounds v Ethylo chloride of Tri METHYL AMINE

METHYL ETHYL ISOAMYL-AMINE C_sH₁₀N * 6 MeNEtC₅H₁₁ (135°) Formed, together with ethylene, by the dry distillation of methyl di ethyl isoamyl ammonium hydroxide MeNEt₂(O₂H₁₁)(OH), which is obtained by the action of moist Ag.O on the product of the

union of MeI with di ethyl isoamyl amine (Hof mann, C J 4, 317) Fragrant liquid, sl sol. orange yellow needles, v water —B'2H2PtCl. sol water

METHYL ETHYL-AMYL-PHENYL-AMMO NIUM HYDROXIDE v Methylo hydroxide of ETHYL ISOAMYL ANILINE, vol 11 p 476

METHYL - ETHYL - ANILINE C.H .: N & & C.H. NMeEt (201° uncor)

Formation -1 By methylation of ethyl anılıne (Hofmann, A 74, 152) -2 By ethyla tion of methyl aniline (Claus a Howitz, B 17, 1325) -3 From di ethyl aniline methylo iodide

Properties —Crystalline, forming extremely able salts The hydrochloride melts at soluble salts

114° (Claus a Hirzel, B 19, 2785)

Methylo-rodide B'MeI [125°], identical with di methyl aniline ethylo iodide (Claus a Rautenberg, B 14, 620, Hjortdahl, J 1882, 510) Triclinic crystals, v sol water and alcohol De composed by boiling with cone KOHAq, yield ing dimethylaniline — B'HCl [114°], very hygroscopic crystals —(B'MeI)₂ZnI₂ monoclinio crystals -(B'Me), H, Fe, Cy, 2aq (Fischer, A 190, 187)

Ethylo rodide B'EtI [102°], identical with di ethyl aniline methyloiodide, by treat ment with KOH it gives methyl ethyl aniline

Propylo iodide C, H, NMeEtPrI Methyl propyl and ne ethylo rodide, ethyl propyl and line methylo rodide. Thick syrup, v sol water Formed by the combination of methyl ethyl ani line with propyl iodide, of ethyl propyl aniline with methyl iodide, or methyl propyl aniline with ethyl iodide. By boiling with aqueous KOH the propyl group is split off and methylethyl aniline regenerated (Claus a Hirzel, B 19, 2785)

Reference - Bromo METHYL ETHYL ANILINE METHYL ETHYL ARSINE v ARSENIC COM POUNDS, ORGANIC

DIMETHYL ETHYL AZONIUM CHLORIDE C4H13N2Cl 2 & Me2NEtCl NH2 Crystalline com pound E sol water Prepared by the combi nation of ethyl chloride with dimethyl hydrazine On reduction with zinc dust and acetic acid it gives dimethyl ethylamine, NH, and HCl (Re nouf, B 13, 2172) -(C,H,,N,Cl),PtCl, crys talline

METHYL ETHYL BENZENE v ETHYL-TOLU

D1 methyl-ethyl-benzene v ETHYL-XYLENE Laurene C₁₁H₁₆ (Laurel) (188°) S G, 887 According to Armstrong a Miller (B 19 887 16, 2258) this liquid is di methyl ethyl benzene C₆H₃Me₂Et [1 2 4] It is one of the products of the action of ZnCl2 on camphor (Fittig, A 145, 149) It yields di methyl benzoic acid on oxi dation Montgolfier (A $\tilde{C}h$ [5] 14, 91) described laurene as $C_{10}H_{14}$ (195°) Reuter (B 16, 627) laurene as C₁₀H₁₄ (195°) Reuter (B 16, 627) described two laurenes (a) laurene (190°) yield ing C₄H₂Me₂CO₂H [1 4 2] on oxidation by dilute HNO_{\bullet} and (β) laurene (185°) yielding on oxidation C.H.MerCO.H [134] and forming a sulphonic acid whose Ba salt is more soluble than that of (a) laurene According to Uhlhorn (B 23, 2346) laurene contains (1,2,4)- and (1,4,2)-di-methyl ethyl-benzenes

O METHYL-ETHYL BENZENE HEXAHY. CH₂CH₂CHMe CHEt DRIDE C.H. . .

-Methyl-ethyl hexamethylene (151°) Formed by boiling CH₂ CH₂ CH₂ CH₂ CH CH(OH) CH₃ with fuming HIAq, diluting with water, extract ng with ether, and heating the resulting oily OH₂ CH₂ CHMe CH CHI CH₃ (179° at 110 nm) with excess of HIAq (8 G 196) and amorphous phosphorus for 8 hours at 235° Kipping a Perkin, jun, C J 57, 26) Mobile Mobile nl with odour of paraffin, miscible with alcohol and ether

o METHYL ETHYL - BENZENE (β) SUL PHONIC ACID C.H. MeEt SO.H [1 2 4?] Formed by sulphonating o ethyl-toluene (Claus a Piesz cek, B 19, 3087) Crystalline - NaA'aq plates, v sol water, insol alcohol — KA'aq plates, v sol water — CaA', 2aq plates grouped in sol water — CaA'₂ 2aq plates grouped in nodules, v e sol water —BaA'₂ 3aq plates, v s sol water —PbA'28aq plates, v e sol water -CuA', aq blue plates, v e sol water

Chloride C.H.MeEt SO.Cl Oil

Amide C6H3MeEt SO2NH2 Yellowish brown oil, v sl sol cold water, sol hot water

m Methyl ethyl-benzene sulphonic acid v

vol 11 p 524

(1, $\hat{2}$, 4) Di-methyl-ethyl-benzene sulphonic acid $C_0H_2Me_2Et$ SO_3H Formed by sulphonating sthyl-o xylene (O Jacobsen, B 19, 2516, Stahl, B 23, 991) Large tables — BaA'₂4aq — BaA'₂3aq white plates, m sol hot or cold water (S) —NaA'1½aq Small white plates, v sol water

Amide C6H2Me2Et SO2NH2 [126°] Long slender needles (from warm, very dilute, alcohol),

or large prisms (from alcohol)
Di-methyl-ethyl-benzene sulphonic acid CaH2Me2Et SO3H Laurene sulphonic acid Formed by sulphonating laurene According to Reuter it is accompanied by an amorphous iso meride which forms a gummy Ba salt Triclinic crystals (Reuter, B 16, 627) When steam is passed into its solution in dilute H2SO4, hydro lysis begins when, through concentration, the temperature has reached 120° (Armstrong a Miller, C J 45, 148) —BaA'₂ 3aq S (of BaA'₂) 2 5 at 16°

Amide C₆H₂Me₂Et SO₂NH₂ [127°] (R) (1, 3, 4) Di-methyl-ethyl-benzene sulphonic acid C₆H₂Me₂Et SO₈H Formed by sulphonating ethyl m-xylene (J) —BaA'₂ 2aq

lamine - NaA'2aq prisms
Amido C₂H₂Me₂Et SO₂NH₂ [148°]

(1, 4, 3) Di-methyl ethyl-benzene sulphonic acid C.H.Me.Et SO.H Formed by sulphonating ethyl p xylene (Jacobsen, B 19, 2516) Large plates (from dilute H2SO4) -NaA'aq mass of large tables (from warm saturated solution) -KA' aq flat needles, v sol water —BaA'2 long sıx sıded plates, sl sol cold, m sol hot, water $-CuA'_28aq$ light blue needles (Stahl, B 23,

Amide C,H2Me2Et SO2NH2 [117°] Pearly plates (from dilute alcohol), or large transparent crystals (from warm alcohol), v sol hot alcohol

METHYL DI ETHYL BORATE MeEt.BO. (100°-105°) SG 2 904 Formed by heating MeBO, with absolute alcohol at 100°

PENTA METHYL ETHYL BROMIDE Tert HEPTYL BROMIDS.

METHYL-ETHYL-BROMANILINE v Bromo-METHYL ETHYL ANILINE

METHYL-ETHYL-CARBINOL v Sec BUTYL-ALCOHOT.

Methyl-di-ethyl-carbinol v Tert HEXYL ALCO-HOL

Di-methyl-ethyl-carbinol v Tert AMYL ALCO

METHYL ETHYL CARBONATE MeEtCO. -14 5°] (109° cor) (Rose, A 205, 230) S G Obtained by distilling a mixture of 27 1 002 potassium methyl carbonate with potassium ethyl sulphate (Chancel, C_a R 31, 521, A 79, Formed also by the action of NaOMe on ClCO₂Et, or of NaOEt on ClCO₂Me (Schreiner, J pr [2] 22, 354)

PENTA-METHYL-ETHYL CHLORIDE v

HEPTYL CHLORIDE

METHYL ETHYLENE v PROPYLENE Di-methyl-ethylene v BUTYLFNE Tri-methyl-ethylene v Amylene Tetra-methyl-ethylene v Hexylfne

METHYL ETHYLENE DIAMINE Nitroderivative C₂H₄(NH NO₂)(NMeNO) Formed by the action of methyl iodide on ethylene dinitramine (Franchimont a Klobbie, R T C 7, 343)

Di'- methyl - ethylene - diamine Nitro derivative C₂H₄(NMe NO₂)₂ [137°] Formed like the preceding

Di methyl ethylene diamine v ETHYLENE

METHYL - ETHYLENE - TRI - ETHYL -

PHOSPHAMMONIUM BROMIDE v vol 11 p DI METHYL-ETHYLENE GLYCOL v

TRI-METHYL-ETHYLENE GLYCOL v Dr

DI METHYL ETHYLENE DIKETONE v

ACETONYL-ACETONE DI-METHYL-ETHYLENE DIKETONE DI CARBOXYLIC ACID v Dr aceto succinic ether

described under ACETYL SUCCINIC FTHER TETRA-METHYL-ETHYLENE-DI-PHENYL-DIPHOSPHONIUM BROMIDE v Ethylenobromide of Phenyl DI METHYL PHOSPHINE

DI METHYL-ETHYLENE DI PHENYL-DIPYRROLE DICARBOXYLIC ETHER

 $C_2H_4(C_4NHMePh\ CO_2Et)_2$ [197°] Formed from acetophenone acetoacetic ether and ethylene diamine (Paal a Schneider, B 19, 3156) Scales (containing 4aq) Yields on hydrolysis the corresponding acid [181°

METHYL-ETHYLENE-PYRIDINE TETRA HYDRIDE C.H., N ie C.H., NMe(C.H.) Tro prdine (162°) SG 2 9665 Formed by heat ing atropine or tropine with fuming HClAq and HOAc at 180°, or by heating tropine with H, SO, (Ladenburg, A 217, 117) Liquid, smelling like conine, v e sol cold, sl sol hot, water, v e sol alcohol and ether Alkaline in reaction Its hydrobromide is decomposed by bromine at 175° yielding di bromo methyl pyridine and ethylene — B'₂H₂PtCl₄ — B'HAuCl₄ — B'HI₄ [98°] Brown prisms — B'C₄H₄(NO₂),OH yellow needles (from boiling water)

Methylo rodide B'MeI Cubes Decomposed on distillation with KOH yielding tropilene C₇H₁₀O, an oil C₅H₆O (?) (202°-207°), dimethylamine and methyl tropine With moist AgeO it gives a syrupy base which yields the salts $(B'MeCl)_2PtCl_1 - B'MeBr - B'MeC_8H_1(NO_2)_0$ TETRA METHYL , ETHYLENE DI PYR-

ROL C, H20N2 1 e CH CMe MeC CH N C₂H₄ N [126°] CH CMe∕ MeC CH

tained by adding ethylene diamine (1 mol) to a solution of acetonyl acetone (2 mols) in an equal weight of absolute alcohol White pearly plates Sublimable Volatile with steam sol alcohol, ether, benzene, and petroleum spirit, insol water Colours a chip of pine wood carmine red Gives a purple red colouration with phenanthraquinone and H2SO, (Paal a Schneider, B 19, 3157)

ETHYLENE DISJLPHIDE DI METHYL $C_4H_{10}S_2$ re $C_2H_4(SMe)_2$ Do methyl ether of di thio glycol (183°) Formed from ethylene bromide and NaSMe (Ewerlof, B 4, 716)

DI METHYL ETHYLENE DISULPHONE v Do methyl ether of Ethane disulphinic acid METHYL ETHYLENE ψ THIO UREA

CH₂ N Methyl CH₂S C NMe or ÓH, NH∕ ımıdo thiazole tetra hydride Methyl amido thiazole dihydride [90°] Formed, together with a crystalline compound C₆H₁₁N₃O₂ [70°], by the action of methyl thiocarbimide on bromo ethylamine (Gabriel, B 22, 1148) Needles, v e sol water, v sol ordinary solvents Strongly Oxidised by bromine water to an acid (? NHMe CO NH, CH CH, SO3H), which is de composed by fuming HClAq at 155° into CO., methylamine, and taurine—Picrate [226°] needles -Aurochloride needles -Platino-

Methyl ethylene ψ thiourea

chloride needles

CH₂ S

CH₂-S C NH Imulo methyl - thiazole CH₂ NMe Formed by heating ethylene ψ this urea with methyl iodide (Gabriel) Oil When it is oxi dised by bromine water it yields methyl taurine NHMe CH, CH SO₃H Salts -B'HI [160°] Colourless crystals, sol water and alcohol-[200°-203°] —The aurochloride Picrate and platinochloride form long needles, sol boiling water

METHYL ETHYL ETHER v METHYL ETHYL OXIDE

METHYL-ETHYL-ETHYLENE v AMYLENF METHYL-ETHYL-GLYOXAL v METHYL ETHYL DIKFTONE

METHYL-ETHYL-GLYOXALINE C.H. N. 2 6 NEt CH

C₃H₂(CH₃)(C₂H₅)N₂ or CH₃ C Oval-ĊН

8 G 15 98 (213°)Formed ethyl ethyline by the action of ethyl bromide on methyl glyoxalıne (glyoxal ethyline) (Radziszewski, B Formed also from di ethyl oxamide NHEt CO CO NHEt by treatment with PCl, and heating the hydro iodide (10 g) of the resulting 'chloroxalethyline' C₆H₂ClN₂ with HIAq (7 g of S G 19) and amorphous phosphorus (1 g) for 6 hours at 140° The product is dissolved in water, rendered alkaline, and extracted with chloroform (Wallach, 4 214, 298) Colourless liquid, with narcotic smell. Sol. water and

alcohol AgNO, gives a crystalline pp , HgCl, a white pp The zinc double chloride forms crystals melting at [160°] Burns with a blue flame It is a strong base and ppts metallic oxides from their salts. Its zinc double salt distilled with lime yields pyrrole, ammonia, HCy, ethylene, and methyl glyoxaline (para oxalmethyline) (Wallach, A 214, 305) It acts physiologically like atropine (Schulz, B 13, 2353) When heated in a sealed tube with dilute H₂SO, at 240° it yields ethylamine KMnO, yields oxalic acid, NH, and acetic acid When passed through a red hot tube it yields HCy and methyl glyoxaline (para oxal methyl ine) H_2O_2 oxidises it to ethyl oxamide (Radzi szewsky, B 17, 1290)

Salts -B'HCl deliquescent crystals -

Crystals, e sol water and alcohol Not decomposed by aqueous NaOH — C₆H₁₀N₂MeI₃
Benzylo chloride C₆H₁₀N₂C₆H₅CH₂Cl

Methyl - ethyl - glyoxaline C₆H₁₀N₂

NMe CH EtC Oxalmethylpropyline The `N ---- ĊH

methylo 10dide B'MeI of this body is formed by the action of MeI on para ethyl glyoxaline (Radziszewsky, B 16, 490)

References - DI BROMO, and METHYL ETHYL GIYOXALINF

METHYL ETHYL GLYOXIM v OximMETHYL ETHYL DIKETONE

METHYL ETHYL HYDROXYLAMINE HYDROXYLAMINE DERIVATIVES

METHYL ETHYLIDENE ETHYL KETONE C,H12O2 1 e CH3 CO CHMe CO C,H3 Acetyl propionyl ethane (167°-170°) Formed by the action of NaOEt on a mixture of di ethyl ketone and acetic ether (Claisen a Ehrhardt, B 22, 1009) Colourless cal —Cu(C $H_{11}O_2$), Blue crystals (from benzene ligroin)

METHYL ETHYLIDENE DI ETHYL SULPHONE v DI ETHYL PROPYLIDENE DI SULPHONE

DI METHYL ETHYLIDENE DI-INDOLE $C_{20}H_{20}N_2$ i e CH $(NH < C_{Me}^{C_6H_4}>C)_2$ CHMe $CH_3 CH(C_8H_3MeN)_2$ Ethylidene methyl [191°] Formed by heating methyl indole (methyl ketole), paraldehyde, and ZnCl2 on the water-bath (Fischer, A 242, 376) Colourless prisms, v sol alcohol, ether, and

acetone DIMETHYL ETHYLIDENE DIKETONE

(CH₃ CO)₂CHMe (165°) Formed from sodium methylene dimethyl diketone and MeI (Combes, C R 105, 868)

METHYL ETHYL INDAZINE C10H12N2 16

.CMe C.H. NEt Formed by heating methyl-

indazine with EtI at 100° (Fischer a Tafel, A 227, 303) Liquid, m sol water, v e sol alco hol and ether, volatile with steam -B'HCl needles

 $C_{\bullet}H_{\bullet} < CMe > N$ Methyl ethyl-180 indazine Formed by Ethyl-quinasole [80°] (235°)heating its carboxylic acid at 160°-190° (Fischer a. Kuzel, A 221, 285, B 16, 655) Formed

also by reducing the nitrosamine of ethyl amido acetophenone, dissolved in dilute acetic acid, with zinc dust, adding NaOH, and distilling with steam The oily distillate is dissolved in dilute H₂SO₄, mixed with NaNO₂, and extracted with ether (Fischer a Tafel, A 227, 303) Plates, sl sol water, v e sol alcohol and ether Vola tile with steam, giving off a pungent odour Not affected by nitrous acid or by Ac₂O Does not reduce Fehling's solution Forms crystalline pps with AgNO, and HgCl2, which may be recrystallised from hot water in slender needles Its salts are extremely soluble in water — $B'H_2SO_4$ long needles — $B'_2H_2PtCl_6$ sparingly soluble orange prisms — Picrate yellow needles

Methylo-rodide B'MeI [192°] METHYL-ETHYL-ISO INDAZINE CARB-OXYLIC ACID C.H. NEt N

Formed by treating the nitrosamine of ethyl-oamido cinnamic acid with zinc dust and acetic acid (Fischer a Kuzel, A 221, 285) Colourless plates [131°] (from water) or groups of smaller plates [126°] (from chloroform ligroin) Sl sol water, v sol alcohol, ether, and chloroform Combines with alkalis and with acids not reduce boiling alkaline solutions of silver or With bromine in HOAc it forms a bromo derivative [173°] and a di bromo-derivatave [196°

METHYL-ETHYL-INDOLE C,1H,1N v.e $C_6H_4 < \stackrel{CEt}{\sim} CMe$ (292° 1 V) Formed by heating the phenyl hydrazide of methyl propyl ketone with ZnCl, at 180° (E Fischer, B 19, 1565, A 236, 132) Yellowish oil, v sl sol water, v sol alcohol and ether Its picrate erystallises from hot benzene in dark red needles With NaNO₂ and HOAc it yields a nitrosamine

 $C_6H_4 < CH_{NEt} > CMe$ Methyl - ethyl - indole Ethyl-methyl ketole (288° 1 V) Formed, together with a base boiling at 256°, by heating methyl indole (methyl ketole) with Etl and alcohol at 100° (E Fischer a Steche, B 20, 2199) Oil, insol dilute acids Colours pinewood red —Picrate [146°] Slender darkred needles (from benzene)

 $C_eH_eMe < CH_{NEt} > CH$ Methyl-ethyl-indole

Ethyl p tolindole (254°) Formed by heating its carboxylic acid for some time at 205° (Hegel, 4 232 218) Oil. volatile with steam Resim-A 232, 218) Oil, volatile with steam Resinified by conc H₂SO₄ Colours pine wood moist ened with HCl red Fuming HNO₂ gives a red colour and a pp

Di-methyl-ethyl-indole C12H15N t.e.

C₆H₄ CMe CMe (281°) Formed by heating bromo levulic (bromo acetyl propionic) acid with Yellowish ethyl aniline (Wolff, B 21, 3363) oil, v sol ether, alcohol, and benzene, sl sol water -Picrate $B'C_6H_2(NO_2)_8OH$ [105°] Red needles, m sol benzene

METHYL-ETHYL-INDOLE CARBOXYLIC ACID $C_{12}H_{12}NO_2$ so $CH_1C_2H_2 < CH_3 > CO_2H$ [202°] Formed from the p tolyl-ethyl-hydrazide of pyruvic acid by warming with dilute (10 p c.)

HClAq, or with phosphoric acid (Hegel, A 282, 218) V sol alkalis, ether, and benzene, insol ligroin With NaOCl it yields a chloro derivative, which is converted by boiling water into methyl ethyl ψ -ısatın

PENTA-METHYL-ETHYL IODIDE v HEPTYL IODIDE

METHYL ETHYL-ISATIN v ISATIN METHYL-ETHYL-KETOLE METHYL ETHYL INDOLE

METHYL ECHYL KETONE C4H8O 10 OH, CO CH, OH, Methyl acetone Mol w 72 (81°) (F a D), (78° at 740 mm) (Schramm, B 16, 1581) S G 13 8125 (F a D), 22 8045 (S).

Formation -1 By the action of ZnEt, on acetyl chloride, or of ZnMe2 on propionyl chlor ide (Freund, A 118, 3, Popoff, A 145, 289) --2 By boiling methyl acetoacetic ether with potash (Frankland a Duppa, A 138, 336), or dilute H₂SO₄ (Böcking, A 204, 17) —3 Among the products of the distillation of crude calcium acetate (Fittig, A 110, 18) - 4 By distilling a mixture of calcium acetate and calcium pro pionate (Schramm, B 16, 1581) -5 By the oxidation of sec butyl alcohol (Kanonnikoff a Saytzeff, A 175, 377) -6 By the action of H_2SO_4 on crotonylene (Lwoff a Almédingen, Bl[2] 37, 493)

Properties - Colourless liquid, smelling like acetone, miscible with water and alcohol With hydrogen sodium sulphite it forms the compound

MeCEt(OH) SO, Na jaq (Fittig)

Reactions —1 Sodium converts it into homo logues of mesityl oxide, of phorone, and of pinacone (Lawrenovitch, B 8, 767) Sodium, added to its solution in benzene, forms an oil C₁₂H₂₀O, smelling like camphor -2 Chromic acid in HOAc oxidises it to acetic acid -3 PCl. yields di chloro-butane CH, CH2 CCl2 CH, treating this body with alcoholic potash at 170° there is formed CH, CH, CH, which ultimately changes into the isomeric CH, C C CH, which yields hexa methyl benzene on condensation with H₂SO₄ (Favorsky, Bl [2] 43, 112) - 4 On warming with pyrrol, MeOH, and a little hydro chloric acid, there is formed a butylidene pyrrole C=CH

body, when crystallised as C15H22N2 5aq, melts at 80°, but when anhydrous it melts at 142° With alcoholic AgNO₃ it yields slender needles of B'₂AgNO₃ (Dennstedt a Zimmermann, B 20, 2454)

Ozim CH, CH, CH, CH (153° cor) SG 24 9195 Formed by the action of an aqueous solution of hydroxylamine on methyl ethyl ketone (Janny, B 15, 2779) Colourless liquid, soluble in ten volumes of water, miscible with alcohol and ether Concentrated NaOHAq forms a crystalline Na salt

Reference - HEXA-BROMO-METHYL-ETHYL KE-

Methyl ethyl diketone CH, CO CO CH, CH, Diketopentane Acetyl propionyl (108°) S 7 at 15° Formed by the action of amyl nitrite on its mono-oxim (nitroso-di-ethyl ketone) (Manasse,

B 21, 2177) Formed also from ethyl aceto acetic ether by saponfying with dilute (3 pc) alkali, treating the product with NaNO₂ and H₂SO₄, removing alcohol by distillation, adding dilute H₂SO₄ (15 pc) and distilling with steam (Von Pechmann, B 21, 1411, 2140) yellow liquid, smelling like quinone, v sol ordi Forms an unstable compound nary solvents Reacts with aniline, forming a with alcohol compound crystallising in needles and melting at 137° Aqueous NaOH converts it into a 'quinogen,' and finally into a quinone [112°], which may be reduced to a hydroquinone [220°], and yields a phenyl hydrazide [225°]

(a) Oxim CH, C(NOH) CO C,H, Isomitroso & ethyl ketone [59°-62°] Formed by the action of amyl mitrite and NaObt upon diethyl ketone (Claisen a Manasse, B 22, 528) Colour

less plates

(Å) $Oxim CH_a CO C(NOH) C_2H_a$ Isomtrosomethyl propyl ketone [55°] (183°-187° cor) Formed by the action of KNO₂ and H,SO₄ on ethyl acetoacetic ether (V Meyer a Zublin, B 11, 323, 695) Crystals, v e sol alcohol and ether m sol cold water Dissolves readily in alkalis, forming a yellow solution

Di oxim CH₃ C(NOH) C(NOH) C₂H₅ [170°] Formed by the action of hydroxylamine on the mono oxim (Schramm, B 16, 180, 2187) Small white needles May be sublimed —C₅H₉N₂O Na white pp

Dr acetyl derivative of the dr oxim CH, C(NOAc) C(NOAc) CH, Prisms, v sol

alcohol and other, sl sol hot water

(a) Oxim (β) phenyl hydrazide CH₂ C(NOH) C(N HPh) CH [128] Formed from the (a) oxim by treatment with pnenylhydrazine (Otte a Pechmann, B 22, 2119) Crystallises from benzene and ligroin

(β) Orim (a) phenyl hydrazide CH₂C(N HPh) C(NOH) C₂H₃ [131°] Formed from the (β) oxim and phenyl hydrazine (Otte a Pechmann, B 22, 2118) Crystallises from benzene and ligrom

(a) Phenyl hydraside

CH, C(N HPh) CO C H₃ [103°] Formed by the action of phenyl hydroxime on the diketone (Otte a Pechmann, B 22, 2115)

(Otte a Pernmann, B 22, 2115)
(β) Phenyl hydrazide

CH, CO C(N HPh) C H, [117°] Formed by saponifying ethyl acetoacetic ether by allowing it to stand with aqueous KOH, then adding di azobenzene chloride, and ppg by sodium acetate solution (Japp a Klingemann, C J 53, 519, B 21, 550, A 217, 220) Yellow radiating needles or prisms (from benzene)

Di phenyl hydrazide CH_3 C(N,HPh) C(N HPh) C_2H_3 [162°] (J), [166°-169°] (C a M) Formed by the action of phenyl hydrazide, or on the diketone, on the (β) -phenyl hydrazide, or on the (a) oxim (Von Pechmann, B 21, 1414, Japp, A 247, 221, Claisen a Menasse, B 22, 528) Yellow needles (from benzene), sol cold conc H_2SO_4 , forming a brown solution

METHYL-ETHYL KETONE CARBOXYLIG ACID v Methyl acetoacetic Acid

METHYL-ETHYL MALONIC ACID C₂H₁₀O₄ to CH₂ CH₂ CMe(CO₂H)₂ Mol. w. 146 [119°] H C v 67,200 H C p 672,300 H.F Vol. III

| 236,700 (Stohmann, Kleber, a Langbein, J pr. | [2] 40, 210)

Formation —1 By saponifying its ether which is obtained by treating ethyl malonio ether with MeI and NaOEt, or methyl-malonio ether with EtI and NaOEt (Conrad a Bischoff, B 13, 596, A 204, 146) —2 Together with a larger quantity of the isomeric s di methyl suc cinic acid (194°), by reducing the anhydride of di methyl maleïc acid (pyrocinchonic acid) with HI or sodium amalgam (Otto a Beckurts, B 18, 841)

• Properties — Prisms, v sol water, alcohol, and ether At 180° it splits off CO, giving valeric acid CH₃ CH₂ CHMe CO H A solution of its ammonium salt gives pps with FeCl₃ and

with salts of Hg and Pb

Salt — AgA' Sparingly soluble white crystalline pp

Ethyl ether Et₂A" (208°) SG $\frac{15}{15}$ 994 Oil, sol alcohol and ether

METHYL-ETHYL-METHANE v BUTANE Methyl di ethyl-methane v HEYANE

Tri-methyl-ethyl-methane v Tert Hexane METHYL - ETHYL - PENTAMETHENYLYL METHYL KETONE TRIHYDRIDE $\mathbf{C_{10}H_{16}O}$ 1.6

CH₁ CO C | Ethyl methyl-dihydro-CH₂ CH₂ CH₂

pentene methyl ketone (210°-215°) Formed from di methyl butylène diketone dicarboxylic ether (di acetyl adipic ether) by heating with EtI and alcoholic NaOEt. The product is freed from alcohol by distillation, mixed with water, and the oil, which can then be extracted by ether, hy drolysed by boiling alcoholic potash (Marshall a Perkin, C. J. 57, 252)

Perkin, C J 57, 252) Oxim $C_{10}H_{17}NO$ Oil METHYL-ETHYL-PENTAMETHYLENE

 $C_{\bullet}H_{16} \approx CH_{2} CH_{2} CHMe$ $CH_{2} CHEt$ (124°) Formed

by heating methyl iodo ethyl pentamethylena (obtained from methyl pentamethylenyl methyl carbinol and HI) with amorphous phosphorus and HI at 245° (Marshall a Perkin, jun, C J 57, 250) Limpid oil, attacked by bromine with difficulty Rapidly oxidised by boiling dilute HNO.

METHYL ETHYL OXIDE C₃H₄O 16 CH₃ O C₂H₅ Mol w 60 (11°) S G 2 7252 (Dobrner, A 243, 2) S V 84 0 (D) V D 2 158 H F p 58,450 (Thomsen, Th) H F v 56,420

Formation —1 By the action of MeI on NaOEt or of EtI on NaOMe (Williamson, P M 13, 37, 350 C J 4, 106, 229) —2 By distilling potassium methyl-sulphate with KOEt (Chancel, C R 31, 152) —3 By the action of Ag₂O on a mixture of MeI and EtI (Wurtz, J 1856, 563) —4 Together with Me₂O and Et₂O by etherification of a mixture of methyl and ethyl alcohols by $\rm H_2SO_4$ (Williamson, of Norton a Prescott, Am 6, 244)

Properties — Colourless mobile liquid, with ethereal odour

METHYL-ETHYL-OXY- v. OXY METHYL-ETHYL METHYL-ETHYL-PHENOL C,H₁₂O 1.6

METHYL-ETHYL-PHENOL C₂H₁₂O 1.8 CH₂C₂H₂Et OH (215°) Prepared by fusing p methyl-ethyl-benzene sulphonic acid with potash, dissolving the product in water, acidifying, and extracting with ether (Mazzara, G 10, 256). Oil, si sol water. Gives an azure blue

colouration with FeCl,

C_eH₂Me₂Et(OH) Di methyl ethyl-phenol Obtained by potash-[6 8 1 2]? [87°] (245°) fusion from the corresponding di methyl ethyl benzene sulphonic acid (Stahl, B 23, 990) FeCl₂ gives an intense green colour in alcoholic (not in aqueous) solution

METHYL - ETHYL - PHENYL - AMINE $\,v\,$

AMIDO TOLYL ETHANE

Tri-methyl-di-ethyl-phenyl-amine C₁₃H₂₁N se C₆Me₅Et₂ NH₂[1 2 5 3 6 4] (286°-290°) S G 971 Colourless oil Obtained by heating a mixture of mono and di ethyl pseudo cumidine with an equal weight of ethyl iodide at 260°-280° for 8-10 hours (Ruttan, C J 49, 813, B 19, 2383)

Salts —B'HCl needles, easily sol alcohol, sl sol hot water, insol cold water The acetate and sulphate form easily soluble needles The oxalate forms very sparingly

soluble quadratic prisms

Acetylderivative CoMesEt, NHAc [182],

DI-METHYL-DI-ETHYL-p PHENYLENE-DIAMINE C₁₂H₂₀N₂ ie C₄H₄(NMe₂)(NEt₂) (265°) Prepared by heating di ethyl p phenyl ene diamine with methyl alcohol and HCl (Lipp mann a Fleissner, M 4, 788) Light yellow oil

Di-methylo di nodide B"Me, I, [218°] Formed by heating di ethyl amido benzene azo di ethyl aniline with MeI Transparent four-B"Me,PtCl₈ orange redneedles —B"(MeAuCl₄)₂ vellow leaflets —B"2MeOC₈H₂(NO₂)₈ [235°] Yellow needles

DI METHYL ETHYL PHOSPHATEC, H11PO te Me_EtPO, (203° cor) S G º 1 1752
161 1 (Lossen, A 254, 74) Formed
Me_AgPO, and EtI (Weger, A 221, 90) Formed from

METHYL-DI ETHYL-PHOSPHINE e Et₂PMe (111°) Formed by heating tri ethyl phosphine methylo chloride Et₃PMeCl at 300° (Collie, C J 53, 719) Combines with sulphur and with oxygen Forms red crystals

with CS.

Methylo-chloride v Ethylo chloride of Di methyl ethyl phosphine

Ethylo iodide v TRI ETHYL PHOSPHINE

METHYL IODIDE Di methyl ethyl phosphine MeaPEt Formed by heating Me, PEtHCl (the product of the distillation of its ethylo chloride) with aqueous NaOH (Collie, $C\ J$ 53, 720)

Methylo chloride v Ethylo chloride of

TRI METHYL PHOSPHINE

Ethylo chloride Me₂PEt₂Cl Formed from Me₂PEt₂I, the product of the union of Et₂PMe and MeI Split up by heat into ethylene and MezPEtHCl (Collie)

METHYL - TRI - ETHYL - PHOSPHONIUM CHLORIDE v Methylo wodrde of TRI-ETHYL-PHOSPHINE

Di-methyl-di-ethyl-phosphonium chloride v. Ethylo-chloride of Di-methyl ethyl phosphine

Tri-methyl-ethyl-phosphonium chloride v. Ethylo-chloride of TRI METHYL-PHOSPHINE

OCTANE.

METHYL-ETHYL PINACONE v. DI-OXY-

METHYL-ETHYL-PIPERIDINE & METHYL ETHYL PYRIDINE HEXAHYDRIDE

METHYL-ETHYL-PROPIONIC ACID HEXOIC ACID

METHYL-ETHYL-PROPYL ALCOHOL HEXYL ALCOHOL

METHYL-ETHYL-PROPYL-AMINE CaH, N e C₃H₇NMeEt A product of the destructive distillation of the methylo hydroxide of ethylcodeine (Von Gerichten a Schrötter, B 15, 1484) Volatile base, smelling like trimethylamine -B'2H2PtCl6 Long orange needles, v sol water, sl sol alcohol

METHYL ETHYL-PROPYL-CARBINOL

Tert HEPTYL ALCOHOL

METHYL-ETHYL-PROPYLENE & HEXYL-

METHYL-ETHYL-PROPYL-METHANE HEPTANE

DI-METHYL-DI-ETHYL-PYRAZINE

C₁₀H₁₆N₂ re N CMe CEt Ne N Dr ethyl hetme (216° cor) VD 563 (calc 568) Prepared by reduction of the oxim of methyl ethyl diketone (methyl nitroso propyl ketone) Me CO C(NOH) Et with tin and HCl, or with sodium amalgam (Treadwell, B 14, 1461) Colourless oil with narcotic smell and alkaline reaction weak poison Combines with water forming a crystalline hydrate Not affected by MeI, acetic anhydride, or HI Bromine added to its solution in HOAc ppts $C_{10}H_{16}N_2Br_2$ as an unstable yellow compound Very dilute potassium permanganate oxidisesittodi methyl pyrazinedi carboxylicacid

N CMe C(CO₂H) N, which does not yield an anhydride (Oeconomides, B 19, 2524) — B'HCl Large colourless crystals - B' H PtCl₆ Soluble red prisms -B'AgNO₃ Crystals, almost insol cold water, v e sol dilute HNO, (Treadwell, B

14, 2158)

Hydrate B'xaq [43°] Large prisms (by sublimation) Gives up its water in dry air, be

coming liquid

METHYL ETHYL PYRIDINE C.H.IN 10 N CH CH CEt (a) Collidine Mol w 121 S G 9 929 (Richard, Bl [2] 32, 488) 168 929 (Weidel a Pick, M 5, 659) SV 1579 (Ramsay) A base found, together with many others, among the products of the dry distillation of bones (Anderson, P M [4] 9, 145, 214, A 94, 360), of bituminous shale (Greville Williams, C J 7, 97) and of peat (Church a Owen, P M [4] 20, 110) It occurs in coal tar Colourless oil, with unpleasant odour Fumes with HCl V sl sol water, separating again when warmed, v sol alcohol, ether, and oils Ppts ferric, alu minium, chromium, and mercurous oxides from their salts, but not manganese and nickel oxides Its salts are deliquescent and gummy KMnO oxidises it to pyridine dicarboxylic (lutidinic) acid [219°], which is converted by heat into pyridine carboxylic acid [302°] -B'2H2PtCla Orange yellow flakes

Ethylo-rodide BEtI Oil -

(B'EtCl)₂PtCl₄ Sparingly soluble crystalline pp (Anderson, P M [4] 9, 221) 'a'-Collidine C₂H₁₁N (179°-188°) This base, according to Oechsner de Coninck (A Ch [5] 27, 468), accompanies (β) colliding in the product of the distillation of cinchonine with

KOH It is perhaps identical with (a) collidine When 'a' collidine is heated with ethylene chlorhydrin and a little water for a few hours at 100° combination takes place. After removing uncombined collidine and chlorhydrin by shaking with ether, the residue is evaporated in vacuo PtCl, forms with the product an owange yellow pp of {C₈H₁₁N(C H₄OH)Cl}₂PtCl. Boiling water removes HCl, forming oxethyl-s collidine chloroplatints {C₈H₁₀N(C,H₄OH)Cl}₂PtCl. This forms brilliant scales (from alcohol) Oxethyl a collidine forms a gold sstt, B'AuCl, crystallising in thin golden needles (Wurtz, Pr 33, 450, C R 95, 263, Bl [2] 39, 536)

Methyl-ethyl pyridine N CH CEt CMe (8) Collidine (196°) S G 2 966 V D 4 25 (calc 4 19) Obtained by distilling cinchonine or brucine with KOH (Oechsner de Coninck, C R 91, 296, A Ch [5] 27, 469, Bl [2] 37, 457, 42, 100, R T C 1, 132, cf Greville Williams, Tr E 21, Part 2, A Ch [3] 45, 488) Colour less, mobile, highly refractive liquid, rapidly turning yellow on exposure to air Sl sol water, sol alcohol and ether When left in contact with moist air it takes up water (1 mol) but does not form a well defined hydrate Potassium permanganate oxidises it to homo nicotinic acid N CH C(CO H) CMe, cinchomeronic acid

 $N \leq CH C(CO_2H) > C CO_2H$, and formic acid It is very poisonous, a sub cutaneous injection of 1 g paralysing the nerve centres HI reduces it to the hydride $C_3H_{13}N$, and, at 250°, forms a brown oil $C_4H_{19}NI_4$ Sodium in alcohol reduces it to the hexahydride C_8H_1 N (175°-180°)

Salts -B'HCl White deliquescent tables -B'H PtCl₆ S 2 1 at 60° (Richard, Bl [2] 32, 488) Orange led powder, converted by bolling water into B' PtCl₄, a yellow crystalline powder -B'HAuCl₄ -B' H.Cl 3AuCl₃ -B',H.HgCl₄ Minute white needles, sl sol water, insol alcohol

Methyl-ethyl pyridine N CH CET CH CH CET CT CH Aldchyde collidine (176°) S G ♀ 9389 (D) Occurrence —As acetate in fusel oil (Kramer

a Pinner, B 3, 77)

Formation -1 By heating ethylidene chloride with alcoholic or aqueous ammonia for 12 hours at 160° (Kramer, Z [2] 6,568, B 3, 202, Durkopf, B 18, 920) Ethylidene bromide may be used instead of the chloride, the temperature employed being then 125°-140° (Tavildaroff, A 176, 12) -2 By heating an alcoholic solution of aldehyde ammonia at 120° (Baeyer a Ador, A 155, 297) 'Para' collidine, picoline, and lutidine are also formed in this reaction (Vohl, J 1870, 807) -8 By distilling aldol ammonia (aldehydine) (Wurtz, Bl [2] 31, 433) -4 By heating glycol with ammonium chloride for 8 hours at 185°, the yield being from 15 to 20 pc of the theoretical quantity (Hofmann, B 17, 1905) -5 By heating ethylene chloride with ethylamine at 190° (Hofmann, B 17, 1907) -6 By heating paraldehyde with acetamide and P.O. at 1600 (Hesekiel, B 18, 3091) —7 By heating aldehydeammonia with paraldehyde at 220° (Ladenburg a Dürkopf, A 247, 42)

Properties—Oil, with aromatic odour, insol. water and dilute acids, v sol alcohol and ether. Fumes with HCl Oxidised by KMnO, to methylpyridine carboxylic acid N<CH C(CO₂H) CH

and isocinchomeronic acid N CC(CO,H) CH (Durkopf a Schlaugk, B 21, 294, cf Wischnegradsky, B 12, 1506) Bromine forms an oily Fuming HIAq and amorphous compound phosphorus at 140° yield brownish blue prisms of $C_8H_{14}NI_3$ or $C_8H_{12}NI_3$ (Ladenburg, B 14, 232) Sodium, acting on its alcoholic solution, forms a hexahydride Heated for some days at 100° with glycolic chlorhydrin and a little water it forms oxethyl aldehydine, of which the platinochloride, (C_sH₁₁N(C H₄OH)Cl)₂PtCl₄, forms orange crystals (from dilute alcohol) It may be decomposed by H2S, the hydrochloride produced would not crystallise, but it is converted by Ag20

into a caustic base (Wurtz, Pr 33, 448)
Salts—B'₂H₂PtCl₈ [180°] Very unstable trimetric crystals—B'HAuCl₄ [72°] Yellow needles, v sol water (Hesekiel, cf Herzig, M 2, 404)—B'C₈H₂(NO₂)₃OH [157°] Greenishyellow four sided tables

Ethylo rodrde B'EtI Trimetric tables, v sol water and alcohol Yields (B'EtCl)₂PtOl₄ crystallising in needles or prisms

Methyl ethyl pyridine N CMe CH CH (161°) S G 2 9361 Formed by heating (a)-methyl pyridine (a picoline) with Et1 at 280°–300° (Ladenburg a Schultz, A 247, 46, B 20, 2720) Liquid, almost insol water, but takes up water from the air Very volatile with steam. Oxidised by KMnO, to pyridine dicarboxylic acid N C(CO,H) CH CH [226°] Sodium reduces it, in alcoholic solution, to a hexahydride

Salts—B'₂H.PtCl₅ [174°] Triclinic tables, sl sol cold, v sol hot, water, insol alcohol— B'HAuCl₄ [110°] Yellow needles, sl sol. water, v sol ether alcohol

Methyl ethyl pyridine NCH CH CH CH (173°) S G 2 9353, 2° 9218 Formed by heating (a) methyl pyridine with Et1 at 280°–300°, and separated from the preceding by fractional distillation (Schultz, B 20, 2720, Ladenburg, A 247, 46) Colourless hygroscopic liquid, with unpleasant odour, sl sol water Oxidised by KMnO, to pyridine dicarboxylic acid NCH CH CH CO₂H Sodium, added to its alcoholic solution, reduces it to the corresponding hexahydride

Salts —B'.H.PtCl_s [190°] Reddish yellow plates, si sol cold, v sol hot, water, insol alcohol—B'HAuCl, [90°] Yellow needles, si sol cold, m sol hot, water, v e sol alcohol—The phosphomolybdate and bismuthiodide are amorphous, the cadmium iodide and periodide are oily

Faracollidine C.H.i.N. (220°-230°) Formed, together with the collidine boiling at 176°, by heating aldehyde ammonis (Baeyer a Ador, A 155, 307) Liquid, with pungent aromatic odour. Its salts crystallise with difficulty Its ethylocodide is syrupy The platinochloride is amorphous

Isomeride of collidine -- Obtained by the putrefaction at 40° of pancreas (200 g) mixed with gelatin (600 g) and water (10,000 g) After 5 days the liquid is distilled, first with H₂SO₄ and afterwards with baryta The alkaline disand afterwards with baryta tillate is neutralised by HCl, evaporated to dryness, and extracted with alcohol The hydrochloride of the base crystallises from alcohol in trimetric needles The free base is got by adding NaOH to the hydrochloride and shaking with ether (Nencki, J pr [2] 26, 49) —(B',HCl)₂PtCl₄ Flat needles Gives off an odour of xylene when The base is not identical with collidistilled dine (from NH, and ethylidene chloride), for it differs in odour, in the crystalline form of the platino chloride, and in being more soluble in

Isomeride of collidine C₈H₁₁N (202°) S G 987) Occurs in the flesh of putrid cuttle fish (Oechsner de Coninck, C R 106, 858, 1604) Mobile liquid, v sol water, alcohol, and ether Absorbs moisture from the air, becoming brown Deliquescent radiating masses --B'HCl B'₂H₂PtCl_e Deep yellow crystals, almost insol cold water Decomposed by hot water, with for mation of B'2PtCl₄, a pale brown powder — B'2H₂HgCl₄ Small white needles —B'2H₂Hg₃Cl₈ Long yellowish needles

Methylo rodrde B'MeI Slender needles Isomeride of collidine v TRI METHYL PYR-

Di-methyl-ethyl pyridine C₉H₁₃N Parvol-(199° cor) (D a G) SG 9 9419, 🋂 9289 (DaS)

Formation -1 By heating propionic aldehyde ammonia (Waage, M 4, 718) -2 By heat ing methyl-ethyl acrolein ammonia (Hoppe, M 9, 643) -3 By heating propionic aldehyde with acetamide and P2Os (Hesekiel, B 18, 3097) 4 By heating propionic aldehyde ammonia with paraldehyde in sealed tubes for 10 hours at 210° (Durkopf a Schlaugk, B 21, 832) -5 By heat ing propionic aldehyde ammonia (4 g) with pro pionic aldehyde (6.5 g) for 6 hours at 210° (Durkopf a Gottsch, B 23, 685)

Properties —Colourless oil, not turned brown by light and air, with faint and not unpleasant smell M sol cold water, sl sol hot water, v sol alcohol and ether KMnO, oxidises it to methyl pyridine dicarboxylic acid [225°] and

pyridine tricarboxylic acid [318°]
Salts —B'₂H₂PtCl₅ [189°] Large mono clinic crystals, sl sol cold water —B'HAuCl₅ Large mono-Glittering lemon yellow spangles, sl sol cold water Not hygroscopic - B'HHg,Cl, [119°] Long pointed needles, almost insoleold water —B'C₆H₂(NO₂)₃OH [152°] Yellow Yellow plates.

Di-methyl ethyl pyridine C₂H₁₃N (217°)Formed, together with the preceding, by heating propionic aldehyde ammonia with propionic aldehyde at 200° (Durkopf a Göttsch, \hat{B} 23, Colourless liquid, not affected by air and light. Has a faint odour of nicotine alcohol and ether, sl sol water Yields a dimethyl pyridine carboxylic acid on oxidation

Salts -B'2H2PtCl6 [above 270°] Yellowishred needles, sl sol water —B'HAuCl, [140°] Silender lemon-yellow needles, sl sol, water containing HCl.—B'HHgCl. [159°]. Long

glittering spangles or well formed monoclinic crystals, sl sol cold water

Di methyl-ethyl pyridine C₉H₁₃N & e N CMe CH CEt (187°) SG 14 916

13 at 0° Obtained by the action of propionic aldehyde and ammonia on acetoacetic ether (Jaeckle, A 246, 45) Formed also by heating to redness a mixture of potassium di methyl ethyl pyridine dicarboxylate (1 mol) with lime (2 mols) (Engelmann, A 231, 44) Liquid, more soluble in cold than in hot water Its solution has a very bitter taste "MnO4 oxidises it to methyl ethyl pyridine carboxylic acid and uvitonic acid

Salts -B',H,PtCl, [211°] Crystalline pp, v sol, hot water and alcohol -B'2H2Cr2O, [120°] Needles Crystalline pp -Picrate

METHYL-ETHYL PYRIDINE DIHYDRIDE (β) Di-hydro collidine $(200^{\circ}-205^{\circ})$ Formed by heating (3) collidine with HIAq and red phosphorus at 140° (Oechsner de Coninck, Bl [2] 42, 116)

Methyl ethyl pyridine hexahydride C₈H₁₇N Formed by adding sodium to an al (c 177°) coholic solution of (B) collidine (Oechsnei de

Coninck, Bl [2] 42, 116)

Methyl ethyl pyridine hexahydride C.H., N te NH CHM CH, CH₂ Copellidine (164°) SG 2 8653, ½ 8546 Formed from the collidine derived from aldehyde, by reduction in alcoholic solution with sodium (Durkopf, B 18, 920, Ladenburg, A 247, 90) Colourless alka Its physiological line liquid, sl sol water action resembles that of comine, but is weaker

Salts-B'HCl [171°] Colourless needles. v sol water -B'HBr [165°] Tufts of needles -B'HAuCl₄ [104°] Dimetric prisms, v sol hot water —B'2H2PtCl, [147°] Long yellow needles, v e sol water

Acetyl derivative C8H16NAc (254°) SG 2 9787, 21 966

Methyl ethyl pyridine hexahydride

NH CHMe CH₂ CH₂ CH₂ 8550, 20 8410 Form $(147^{\circ}-151^{\circ})$ Formed by reducing the cor responding methyl-ethyl pyridine in alcoholic solution with sodium, the product being purified by means of its oily nitrosamine (Schultz, B 20, 2723, Ladenburg, A 247, 95) Colourless alka line liquid, smelling strongly like ammonia and like piperidine, sl sol water

Salts —B'HCl Needles, v e sol water and

alcohol —B'HBr Needles

Methyl ethyl pyridine hexahydride

NH CHMe CH₂ CHEt Copel 160°) S G ² 8515, ²² 8389 Copellidine (155°-Obtained by reducing the corresponding methyl ethyl pyridine in alcoholic solution with sodium, product being purified by means of the nitros amine (Ladenburg a Schultz, B 20, 2723, A 247, 96) Colourless, strongly alkaline liquid White needles, v e sol -B'HCl [c 213°] water and alcohol

v-Methyl ethyl-pyridine hexahydride NMe CHEt CH OH, (c 149°) 8495 Formed by the action of MeI on the corresponding ethyl-pyridine hexahydride dissolved in MeOH, the product being distilled with strong aqueous NaOH (Ladenburg, A 247, 71) Liquid, smelling like ν methylpyridine hexahydride, al sol water Its hydrochloride crystallises in small needles

Di-methyl-ethyl pyridine hexshydride C.H. N Parpevoline (177°) SG 2 8628, ¥ 8542, 20 8474 Formed at the same time as di methyl ethyl pyridine (199°), when pro pionic aldehyde ammonia and propionic aldehyde are heated together at 200° Formed also by reducing the same di methyl ethyl pyridine by adding sodium to its alcoholic solution (Durkopf a Gottsch, B 23, 690) Very mobile colourless liquid, with penetrating odour like rotten hay, v sol ether and alcohol, sl sol Strongly alkaline in reaction — [120°-130°] White sparingly B',H,CdI, soluble needles (from hot water) -The hydro chloride and hydroiodide are hygroscopic Chlorides of gold and of platinum give no pp in dilute solution, and oily pps in concentrated Picric acid acts in like manner solutions

Di methyl ethyl pyridine hexahydride

C₂H₁₉N ie NMe CH₂CHEt CH₂ V Methylcopellidine (165°) V D (H=1) 139 5 (obs S G ²/₂ 8519, ¹/₄ 814 Formed from methylethyl pyridine hexahydride (164°) and MeI in the cold (Ladenburg a Durkopf, B 18, 925, A 247, 90). Strengtiv all always colourless of all 247, 90) Strongly alkaline colourless oil, sl sol water —B'HBr [151°] White needles -Picrate [162°] Yellow needles

Methylo vodide B'MeI [268°] Long white needles, m sol water, v sol alcohol, ppd by ether from alcoholic solution With moist Ag₂O it yields a methylo hydroxide which is split up on distillation into water and tri methyl

ethyl pyridine

Wethylo chloride B MeCl Formed from the rodide by shaking with AgCl -(B'MeCl) PtCl. Yellow octahedra — (B'MeCl) HgCl [108°] Long white needles

Di methyl ethyl pyridine hexahydride

C9H19N 1 e NH CH VICH CH Parperol-(167°) at 725 mm Ethyl lupetuline Formed by reducing di methyl ethyl pyridine (187°) in alcoholic solution with sodium (Jaeckle, A 246, 45) Liquid Gives, in a dilute alco holic solution, dark brown pps with silver or mercurous nitrate —B'₂H₂PtCl₄ Orange prisms -B',H2Cr2O, Long prisms

Tri methyl ethyl pyridine hexahydride C10H 1N 1 e C2H MeNMe Dr methyl collidine Di methyl copellidine hexahydride SG 7816 Formed by distillation of the methylo hydroxide of v methyl copellidine (di methyl ethyl pyridine hexahydride) (165°) (Durkopf, B 18, 927, Ladenburg, A 247, Colourless alkaline liquid, sl sol water. Smells like trimethylamine —B'HAuCl, Yellow needles or glistening plates -B'2H2PtCl₆ [93°] Silky yellow needles

METHYL ETHYL PYRIDINE CARBOXYLIC $N < C(CO_2H) CH > CEt$ ACID C.H.NO. 16 Formed by oxidising the corresponding dimethyl-ethyl-pyridine with KMnO₄ (Altar, A 228, 189) — (HA')₂H₂PtCl₄ [195°]. Red prisms

Di methyl ethyl pyridine dicarboxylic acid C₁₁H₁₃NO, ie N CMe C(CO₂H) CEt Parvol me dicarboxylic acid ີ່ [**2**90° ∫ Obtained by saponifying its ether with alcoholic potash (Engelmann, A 231, 40) Thick prisms, m sol cold water and alcohol, decomposed on fusion On distillation with lime it yields di methylethyl pyridine —BaA' 3aq Plates, v e sol water — $(H_2A'')_2HCl$ aq Prisms $Ethyl\ ether\ Et.A''$ (305°-308°) Formed

by passing nitrous acid gas into an alcoholic solution of the dihydride Thick liquid -(Et, A"), H, PtCl, [139°] Long prisms (from

alcohol)

DI-METHYL - ETHYL PYRIDINE DIHY. DRIDE DICARBOXYLIC ETHER C13H23NO, 1 e $\mathrm{NH} <_{\mathrm{CMe~C(CO~Et)}}^{\mathrm{CMe~C(CO_2Et)}} >_{\mathrm{CHEt}}$ Hydroparioline dicarboxylic ether [110°] Formed by boiling acetoacetic ether (45 g) with propionic aldehyde (10 g) and alcoholic ammonia (Engelmann, A 231, 38) Prisms (from alcohol), v e sol hot alcohol, ether, chloroform, and benzene

METHYL ETHYL PYRIMIDINE C H, N, 2 e. CEt N CMe CH (160°) Formed by reducing oxy methyl ethyl pyrimidine with zinc dust (Pinner, B 22, 1619) Prisms (Py 2 3) METHYL ETHYL QUINOLINE

C₁₂H₁₃N re C₆H CH CMe N CEt $[56^{\circ}]$ (268° at 710

mm) Formed by the action of propionic aldehyde and HCl upon aniline (Dabner a Miller, B 17, 1714) Large monoclinic prisms V sol alcohol, ether, and benzene, sl sol water On oxidation with CrO, and H2SO, it yields (Py 2)-

methyl quinoline (Py 3) carboxylic acid
Salts -B',H Cl.PtCl, fine yellow needles.
-Picrate B'C,H (NO),OH yellow crystals -B'2H2Cr2O, small yellowish brown prisms

Methylo-rodide B'MeI [196°], yellow needles, insol ether

(B 2) Methyl (Py 3) ethyl-quinoline

CH CH C,H3(CH3) Ethyl toluquinoline. N C(C,H,)

(270° at 718 mm) Formed by heating its (Py 2) carboxylic acid (Harz, B 18, 3395) White needles V sol ether or petroleum-Yields on oxidation ethyl quinoline ether carboxylic acid (Daniel, B 23, 2267)

Salts -B'HClx small white concentric crystals—B'HNO₃* fine white needles—B'₂H₂SO₄* colourless crystals—B'₂H₂Cl₂PtCl₄: fine orange needles, sol hot water, sparingly incold -B'C,H2(NO2),OH [244°], verysparingly soluble yellow microscopic crystals

(B 4-Py 2) D1 methyl-($\dot{P}y$ 3)-ethyl quinol-CH C(CH₃) nne $C_6H_8(CH_8)$ [44°] (280° at · N C(C₂H₈)

717 mma) Formed by the action of propionic aldehyde and HCl upon o toluidine (Harz, B 18, Large colourless monoclinic crystals It is reduced by tin and HCl to a tetra hydride, which is a yellowish oil of boiling point 275° at 724 mm Yields methyl ethyl-quinoline (B 4)carboxylic acid on oxidation

Salts -B'HCl easily soluble fine colour-

less needles — B'HI*, very long colourless needles, v sol. hot water, very sparngly in cold — B'2H₂Cl₂PtCl₄ large plates — B'C₈H₂(NO₂)₈OH: f187°]. nearly insoluble vellow needles

[187°], nearly insoluble yellow needles

Methylo-rodide B'MeI 2aq white needles

Gives (B'MeCl), PtCl, small glistening orange

red needles

(B 10r3 Py 2) Di-methyl (Py 3) ethyl-quinoline $C_aH_a(CH_a)$ (CH_a) [41°] (288°-

292° at 720 mm) Formed by the action of piopionic addehyde and HCl upon m toluidine (Harz, B 18, 3397) Colourless trimetric hexa gonal plates 1t is reduced by tin and HCl to a tetrahydride, which is a colourless oil of boiling

point 282°-285° at 720 mm

Salts—B'HCl× easily soluble colourless prisms—B'HI× long colourless needles, soluble in hot water, very sparingly soluble in cold—B'₂H₂Cl₂PtCl₄ 2aq orange plates or fine needles, sl sol cold water—B'C₆H₂(NO₂)₃OH [220°], yellow needles, sol hot alcohol, nearly insol water

Methylo vodide B'MeI aq yellow needles, ▼ sol hot water, gives (B'MeCl)₂PtCl₄ small glistening orange red crystals

 $(B \ 2 \ Py \ 2)$ D1 methyl $(Py \ 3)$ ethyl quinol-

ine $C_eH_s(CH_s)$ $\stackrel{CH}{\underset{N}{(C(C_2H_s)}}$ [54°] (288° at

720 mm) Prepared by adding propionic alde hyde (60 g) to a cooled mixture of p toluidine (50 g) and strong HCl (90 g), finally heating for a short time on the water bath White trime tric crystals Sparingly volatile with steam V sol alcohol, ether, and benzene, insol water It is reduced by tin and HCl to a tetra hydride (286°) It combines with bromine, forming a dibromide, which crystallises in yellow needles [91°] By CrO₃ and dilute H_2 SO₄ it is oxidised to (B 2) methyl (Py 3) ethyl quinoline (Py 2) carboxylic acid

Salts—B'HCl syrup, which slowly crystallises—B'HBr easily soluble white silky needles—B'HI long colourless needles, v sol hot water, spaningly in cold—B',H,Cr,O, spaningly soluble red needles—B',2H,Cl PtCl, 2aq orange-red needles [208°] (Jungmann, B 23, 2273)—B'C,H_(NO_2),OH [177°], small yellow needles

Methylo vodide B'MeI aq [218°], mono-

clinic yellow crystals

Methylo chloride B'MeCl, colourless soluble needles — (B'MeCl) PtCl, soluble needles — (B'MeCl) PtCl, small

Ethylo vodude B'Etl $\frac{1}{2}$ aq [114°], small yellow crystals —(B'EtCl),PtCl, aq glistening crystals (Harz, B 18, 3384)

References — AMIDO, DI BROMO, NITRO, and OXY-METHYL ETHYL QUINOLINES

Formed from (1,3,4) xylidine, propionic aldehyde and HCl (Waldbott, B 23, 2270) Trichinic tables (from alcohol), gives on oxidation (B 2, Py 3) di-methyl-(Py 3)-ethyl quinoline (B 4) carboxylic acid [183°]—B'₂H₂PtCl₆—B'HCl 3aq—BH₃SO₄ Monoclinic crystals—B'H₂Cr₂O₇—B'HNO₈ Monoclinic crystals (from alcohol-

ether) — $B'C_6H_2(NO_2)_3OH$ [183°], Yellow needles

Methylo-rodide B'MeI Needles

(Py~2,4) Methyl ethyl-quinoline dihydride $C_8H_4 < \frac{CH}{NEt} \frac{CMe}{CH_2}$ (255°) Formed by heating methyl ethyl-indole with MeOH and MeI for 15 hours at 120° (Fischer a Steche, A 242, 363) Oil, forming very soluble salts

Py (2,3) Methyl ethyl quinoline tetrahydride CH₂ CHMe

C₁₂H₁₇N to C₆H, UH₁₂CH_{Me} (262° at 720 NH CHEt

mm) Formed by reduction of (Py 2 3) methyl ethyl quinoline with in and HCl (Doebner a Miller, B 17, 1716) Colourless liquid Fe₂Cl_e gives a red colouration—B'HCl sparingly soluble colourless concentric needles

(Py 3,4) - Methyl - ethyl - quinoline tetrahydride C₁₀H₁ NEt 1 e C₀H₄ | NEt CHMe

(256°) Obtained by reducing $(Py \ 3)$ methyl quinoline ethylo iodide with tin and hydrochloric acid (Moller, $A \ 242,\ 321)$ Colourless liquid — $B_2'H_2PtCl_8$ Red granular crystals, decomposed by boiling water

Methylo iodide B'MeI [187°] Not

acted on by KOHAq

(Py 2,3,4) Di-methyl-ethyl-quinoline dihydride C₁₃H₁₇N is C₆H₄CH—CVe NEt—CHMe

(256° 1 V) Formed by heating methyl ketole (methyl indole) with ethyl alcohol and ethyl iodide for 15 hours at 100° (E Fischer a Steche, A 242, 360, B 20, 2200) Oil The salts are v sol water

Methylo rodide B'MeI [189°] Colour less crystals, sol water and alcohol

D1 - methyl - ethyl - quinoline dihydride C₁₃H₁N (255° 1 V) at 750 mm Formed by heating methyl ethyl ketole (methyl ethyl indole) (1 pt) with MeI (2 pts) and MeOH(1 pt) at 120° (F a S)

(B 4, Py 2) D1-methyl-(Py 3)-ethyl-quinol ine tetrahydride C_8H_3Me NH CHEt

(275°)

at 724 mm Obtained by reducing the corresponding dimethyl ethyl quinoline with tin and HCl (Harz, B 18, 3400) Yellowish oil, sparingly volatile with steam

(B 3? Py 2) D1-methyl-(Py 3)-ethyl-quinol CH₂ CHMe

ine tetrahydride C_cH_sMe | (c 284°)

at 720 mm Obtained by reducing the corresponding dimethyl ethyl quinoline with tin and HCl (Harz) Oil

(B 2, Py 2) Di-methyl-(Py 3)-ethylquinoline CH_2 CH(CH₃) CH_3 (CH₄) CH_4 CH(C₂H₃) CH_5 (286° CH_5 CH(C₂H₃)

at 720 mm) Formed by reduction of di methyl ethyl quinoline with in and HCl (Harz, B 18,

3387) Colourless refractive fluid
Salts —B'HCl colourless needles, sl sol
cold water —B'₂H₂Cl₂PtCl₄ 2aq brown plates
Nitrosamine C₁₈H₁₈N(NO) crystalline

solid, sparingly volatile with steam

(B 2-Py 24)-Tri-methyl-(Py 3)-ethyl-quin- $CH_2 - CH(CH_3)$ eline tetrahydride CaHa(CHa)

N(CH,) CH(C2H,) (275°-280° at 720 mm) Oıl Formed by heating (B 2 Py 2) - di methyl - (Py 3) - ethyl quinoline tetrahydride with methyl iodide- $\dot{B}'_2H_2Cl_2PtCl_4$ 2aq needles (Harz, B 18, 3388) (B 2,4, Py 2) Tri methyl (Py 3) ethyl-

quinoline tetrahydride C14H21N (288°) Formed by reducing the corresponding tri methyl ethylquinoline (Waldbott, B 23, 2272) $B'C_6H_2(NO_2)_3OH$ [146°]

 (\hat{P}^*2) - \hat{M} ėth $\hat{\mathbf{Y}}$ L - $(\hat{P}y$ 3) - eth $\hat{\mathbf{Y}}$ L - Quinol -

INE CARBOXYLIC ACID

CH C(CO₂H) C₆H₃(CH₃) [143°] Formed by $\dot{\mathbf{C}}(\mathbf{C}_2\mathbf{H}_5)$

oxidation of (B 2 Py 2) di methyl (Py 3) ethyl quinoline with CrO_s and dilute \dot{H}_s SO₄ (Harz, B 18, 3392, Daniel, B 23, 2266) Triclinic needles, prisms, or plates (containing aq) Sol water and alcohol Yields on distillation methyl ethyl quinoline [60°]

Salts -A'Na3aq easily soluble glistening crystals -A'Ag granular powder -A'2Ba 3aq soluble needles — A', Cu microcrystalline blue pp Ethyl ether EtA'xaq [170°-190°] De

composed on fusion (Harz, B 18, 3394) Methyl ethyl quinoline (B 4) carboxylic

CH CMe acid CO2H C6H3 [216°] Formed by N ČEt

oxidation of (B 4, Py 2) Di methyl (Py 3) ethyl quinoline (Miller a Daniel, B 23, 2266) Insol water sl sol cold alcohol Gives on dis tillation methyl ethyl quinoline[56°] -BaA', 1aq

 $(B-2,\ P_{V-2})$ Ďi methyl (P_{V-3}) ethyl quin oline (B-4) carboxylic acid $C_{14}H_{14}NO$, i e

CMe CH——C CH CMe [183°] Formed by CH C(CO2H) C N CEt oxidising (B', 2, 4, Py, 2) tri methyl (Py, 3) ethylquinoline by CrO, and H SO, (Jungmann, B 23, 2273) Needles (from alcohol), v e sol alcohol and water, sl sol benzene On dry distillation it gives CO, and (B 2, Py 2) di methyl (Py 3) ethyl quinoline (254°)

 (B^2) METHYL-(Pu 3)-ETHYL-QUINOLINE CARBOXYLIC ALDEHYDE C13H15NO 2 e

CH C CHO C₆H₃Me< [57°] (above 300°) N ČEt

Formed, in small quantity, in the preparation of the preceding acid (Harz, B 18, 3397) Large trimetric prisms (from ether), not very volatile with steam Reduces ammoniacal AgNO, Ag2O oxidises it to the corresponding acid (Daniel, B 23, 2267)

 $(B\ 2^{'}Py\ 2)$ DI METHYL $(Py\ 3)$ ETHYL QUINOLINE SULPHONIC ACID C'13H'11N(SO3H) [above 290°] Formed by heating di methyl ethyl quinoline with fuming sulphuric acid (20 pc SO.) (Harz, B 18, 3389) White silky scales or thick trimetric crystals Easily soluble in hot water, sparingly in cold, insol strong alcohol

Salts -A'Baaq easily soluble white needles -A',H2Pb 6aq easily soluble needles METHYL-TRI ETHYL-RÉSORCIN

O, McEt, (OH). [144°] Obtained by heating with HCl its mono-ethyl derivative C. MeEt. (OH) (OEt)

which is formed, together with the di ethyl ether of orcin, by treating orcin with EtI and KOH (Herzig a Zeisel, M 11, 318) Needles, insol water, v sol ether Neutralises only 1 mol NaOH

Acetyl derivative C6MeEt8(OAc)(OH) [c 73°] Monoclinic needles

METHYL TRI-ETHYL SILICATE C, H, SiO te MeEt, SiO, (156°) S G º 989 Formed from MeO SiCl, by the action of EtOH (Friedel a Crafts, A Ch [4] 9, 32)

Di methyl di ethyl silıcate Me₂Et₂S₁O₄ (143°-146°) V D 6 18 (calc 6 23) S G 2 1 004 Formed from MeOH and Et,SiO, For by the action of EtOH on (MeO),SiCl, Tri methyl ethyl silicate Me,EtSiO, Formed also

(134°) SG 2 1023 Formed from (MeO), SiCl and EtOH

METHYL ETHYL STIBONIUM SALTS v An TIMONY, vol 1 p 294

METHYL ETHYL SUCCINIC ACID

C,H₁₂O₄ re CO₂H CHEt CHMe CO₂H [168 5°] Formed by the action of H2SO4 on pentane tricarbovylic ether (Bischoff a Walden, B 22, It is accompanied by the isomeric 'meso' acid [88°] (Bischoff a Mintz, B 23, 647) The same acid [160°] appears to be formed in small quantities in the saponification of CH₃ CO CMe(CO₂Lt) CHEt CO₂Et with (Young, C J 43, 180) White crystals

Di methyl ethyl succinic acid CoH, O, re CO.H CHEt CMe, CO.H Formed by the action of H,SO, on the product of the action of a bromo isobutyric ether on sodium ethyl malonic ether (Bischoff a Mintz, B 23, 651) It occurs in two varieties, one melting at 63° the other at 105° DI METHYL DI ETHYL-SULPHAMIDE

C₆H₁₆N SO₂ i e O₂S < NMe₂ NEt₂ (229°) by the action of di ethyl amine on di methyl amido sulphonic chloride, or of di methyl amine on di ethyl amido sulphonic chloride (Behrend, B 15, 1610, A 222, 125, 136) Volatile with steam Heavy oil Insol water, sol alcohol, ether, and benzene

METHYL ETHYL SULPHIDE C₃H₂S ι ε S Et (67° 1 V) S G ²⁰ 837 V D 2 61 Me S Et (67° 1 ♥) Formed by distilling an alcoholic (calc 2 63) solution of NaSEt with MeI (Kruger, J pr [2] 14, 193, Claesson, J pr [2] 15, 174, B 20, 8413) Occurs also among the products obtained by heating di thio phosphoric ether Et, PO,S, with MeOH at 150° (Carius, A 119, 313, 120, Liquid, with unpleasant odour ethane sulphonic acid on oxidation with HNO, -EtSMeHgCl, $laminæ (C) - (EtSMe)_2HgI_2$ Yellow crystalline powder

Methylo rodide EtSMe2I v DI METHYL-SULPHIDE ethylo-wodule

Ethylo rodide Et, SMeI v Methylo compounds of DI ETHYI SULPHIDE, vol 11 p 516

METHYL - ETHYL SULPHONAMIDE

METHYL ETHYL-SULPHAMIDE

METHYL ETHYL SULPHONE C3H4SO, te MeEtSO₂ [36°] Formed by oxidising MeSEt with KMnO₄ (Beckmann, J pr [2] 17, 455) Formed also by heating C₂H, SO₂CH₂CO₂H to 190° (Otto, B 21, 993) White needles (from 190° (Otto, B 21, 993) V sol water, alcohol, benzene, chloroform, and strong acids Sl sol CS, and ether Not affected by reducing agents

METHYL ETHYL SULPHONE CARBOXY-LIC ACID C.H.SO. 1 e Et SO. CH. CO.H Ethyl-sulphono acetic acid Obtained by saponifying its ether with cold cone KOHAq Formed also by oxidising the barium salt of the ethyl derivative of thioglycollic acid with KMnO, (Claesson, Bl [2] 23, 447) Thick colourless syrup At 190° it splits up into CO_2 and methyl ethyl sulphone [36°] Bromine added to its aqueous solution gives a di bromo methyl ethyl sulphone Zinc and HCl reduce it to ethyl mercaptan

Salts — NaA' Pearly plates, v si sol hot alcohol, v sol water — KA' Small tables (from alcohol) -BaA'2 Nodules -CuA'2 2aq Broad tables

Ethyl ether EtA' Formed by the action of chloro acetic ether on sodium ethane sulphin ate (Claesson, J pr [2] 15, 223, Otto, \vec{B} 21, 993) Oıl

METHYL ETHYL-THIAZOLE

 $<_{\text{CH CMe}}^{\text{S CEt}} >_{\text{N}}$ (161° cor) Formed by the action of thiopropionamide on chloro acetone in alcoholic solution (Hubacher, A 259, 230) Liquid, smelling like pyridine, miscible with alcohol, insol hot water, al sol cold water -B'2H,PtCl, [177°] METHYL ETHYL DITHIOCARBONATE v

ETHYL THIOGARBONATES, vol 11 p 521

METHYL ETHYL THIO UREA C.H. N.S 26 NHMe CS NHEt [54°] Formed by addition of methylamine to ethyl thic carbinide (Hofmann, B 1, 27, Z 1868, 655) Fine crystals, sol water, alcohol, and HClAq

Methyl di ethyl-thio- ψ urea $C_0H_{14}N_2S$ ι ϵ NHEt C(SMe) NEt Formed from di ethyl thiourea and MeI (Noah, B 23, 2196) Oil With alcoholic NH, at 100° it yields di ethyl guanidine and $MeSH \stackrel{-}{-}B'HI - B'C_6H_2(NO_2)_3OH$ [116°] $-B'_2H_2PtCl_6$ laminæ

METHYL-ETHYL TOLUQUINOLINE v Dr

METHYL-ETHYL-QUINOLINE

METHYL ETHYL UREA C4H10N2O NHMe CO NHEt [53°] (267°) (Wurtz, Rép chim pure, 4, 199) [92°-112°] (Schreiner) Formed from methylamine and cyanic ether When methylamine acts on ethyl-(Wurtz) carbamic ether there is formed a methyl ethylurea which melts at 105° and solidifies again at When, on the other hand, ethylamine acts on methyl carbamic ether the methyl ethylurea which is produced melts at 75° and solidifies again at 72° (Schreiner, J pr [2] 22, 360). After frequent meltings and solidifyings, both these forms begin to melt at 92° and end at

METHYL-EUGETIC ACID v Methyl derivative of EUGETIC ACID

METHYL-ISO-FERULIC ACID v Iso FERULIC ACID and the dimethyl derivative of CAFFEIG ACID, vol 1 p 659

METHYL-FLAVOLINIUM HYDRATE v methylo hydrate of (Py 31) PHENYL METHYL-

QUINOLINE (flavoline)
METHYL-FLUORESCEIN v so-called 'lomo-

fluorescein, vol 11 p 558

METHYL FLUORIDE CH.F VD 1 22
(calc 119) S 1 66 at 15° (D a P) Formed, together with Me2O, by the action of KF on KMeSO₄ (Dumas a Peligot, A 15, 59) Formed also, in small quantity, together with NMe₃, by

heating NMe₄F at 180° in vacuo (Lawson a Collie, C J 53, 628, 55, 110) Prepared by the action of MeI upon silver fluoride (Moissan a Meslans, C R 107, 1155) Gas, sl sol water, v sol alcohol and MeI Liquefied by a pressure of 30 atmospheres It burns with a blue flame. yielding HF Saponified with difficulty by heating in sealed tubes with water or dilute aqueous KOH at 120° In the presence of a little water it forms a crystalline hydrate, decomposing at 18 8° (Villard, C R 111, 184) Chlorine, acting upon it in sunlight, forms CH2ClF, a gas which is decomposed by water, and is hardly inflammable

METHYL FORMAMIDE v Formanide in the article on Formic acid

Di methyl formamidine C3H8N2 28

NMe, CH NH Form-unid di methyl amide Formed by the action of an alcoholic solution of di methyl amine on the hydrochloride of formımıdo ether (Pınner, B 16, 1650) —B'HCl thick prisms, [169°], v sol water and alcohol

s D1 methyl-formamidine NHMe CH NMe Form methyl imid methyl amide Formed by the action of an alcoholic solution of methyl amine on the hydrochloride of formimido ether NH CH OEt -B', H. Cl PtCl, short red prisms, [172°] (Pinner, B 16, 358, 1648)

METHYL FORMANILIDE v FORMIC ACID DI METHYL-FUMARIC ACID v DI METHYL MALEIC ACID

METHYL-FURFURALDEHYDE C, H,O, ve (187° 1 V) C.H.MeO CHO Methyl furfurol S 33 Appears to accompany furfuraldehyde in the product of the dry distillation of wood (Hill, B 22, 607) Formed also by distilling isodulcite with dilute H.SO. (Maquenne, C R 109, 604) According to Bieler a Tollens (A 258, 110, B 22, 3062) fucusol or fucus aldehyde $(q \ v)$ is a mixture of furfuraldehyde and inctive furfuraldehyde Combines with NaHSO, Aque ous ammonia converts it into crystalline methyl furfuramide $N_2(C_0H_0O)_8$ [87°] Yields, on oxida tion, methyl pyromucic acid C₆H₆O₈ [109°] Reduces Ag₂O Gives Schiff's reaction with iosani line and SO₂ Its phenyl hydrazide is liquid With resorein and HCl it yields an orange yellow condensation product Pyrogallol and HCl form a crimson compound Paper moist ened with aniline acetate is coloured yellow, and finally deep orange red by an aqueous solution of methyl furfuraldehyde

OMe CH (aa) DI METHYL FURFURANE CaHaO 2e (94°) CMe CH

Formation -1 By dry distillation of pyro tritaric or carbopyrotritaric acid, the yield being 5-7 pc - 2 By distilling acctonyl acetone CH₂ CO CH₂ CH₂ CO CH₃ with ZnCl₂, the yield being 25 pc (Dietrich, B 20, 1085) -3 Occurs also in the product obtained by distilling sugar (1 pt) with hme (3 pts) (E Fischer a Laycock, B 22, 101)

Properties - Colourless mobile very volatile liquid of characteristic odour Insol water, miscible with other solvents Does not react with phenyl-hydrazine. By PCl, or POCl, it is resinified By heating with soldified water it is converted back into acetonyl-acetone

[138°]

METHYL-FURFURANE CARBOXYLIC ACID METHYL PYROMUCIC ACID

Di methyl-furfurane carboxylic acid v Pyro-TRITARIC ACID

Di methyl furfurane dicarboxylic acid

 $C(CO_2H)$ $C(CO_2H)$ (Knorr, of Fittig, C_aH_aO₅ re ČMe O ČMe

B 18, 3410) Carbopyrotritaric acid Formed by boiling diacetyl succinic ether for a long time with dilute H2SO4 (Harrow, C J 33, 425, A 201, 152) Formed also by the action of fuming HCl on acetonyl aceto acetic ether CH₃ CO CH₂ CH(CO,Et) CO CH₃ (Paal, B 17,

Properties - Needles (by sublimation), m sol hot water, v sol alcohol and ether, volatile On heating above its melting point with steam it is decomposed into CO, and di methyl furfur ane carboxylic acid (pyrotritaric acid) fusion yields acetic and succinic acids

silky needles -BaA" -Salts - K.A" Ag A" white pp HAgA" slender white

needles

Mono methyl ether MeHA" [129°] Formed by leaving a mixture of the di methyl ether (1 pt) and fuming HClAq (10 pts) to stand in the summer time (K a C) Slender needles ---AgMc A" Ppd by adding ammoniacal AgNO, to a solution of McHA"

Di methyl ether Me2A" [64°] From Ag A" and MeI at 100° under pressure (Knorr a Cavallo, B 22, 155) Snow white crystals, v sol alcohol, ether, chloroform, and benzene, v sl sol water, dilute acids, and

alkalıs

Methyl ethyl ether MeEtA" From Ag VeA" and EtI, or from Ag EtA" and McI (K a C) The identity of the ethers pie The identity of the ethers pie pared in these two ways shows that the carboxyls are similarly situated in the molecule of di methyl furfurane di carboxylic acid H A", and the ethers Me A" and Et₂A"

Mono ethyl ether

Formed by heating di acetyl succinic ether at 200°, or by allowing it to stand with conc HClAq for some hours in the cold (Knorr, B 17, 2863) Formed also from AgHA" and EtI (Harrow) Flat glistening needles, v sol alcohol and ether, sl sol water May be distilled AgEtA" Bulky white pp (Knoir a Cavallo, B

 $2\tilde{2}, 154)$

Di ethyl ether Et2A" (275°) at 735 mm Formed by dissolving di acetyl succinic ether in cold H SO4, or by heating it with conc phosphoric acid (Knorr) Formed also, together with pyrotritaric and iso carbo pyrotritaric ethers, by heating discetyl succinic ether at 175° (knorr, B 22, 158) Oil Does not react with hydroxylamine or with phenyl hydrazine Easily saponified by alcoholic potash

Di methyl-furfurane dicarboxylic acid v. METHRONIC ACID

METHYL FURFURINE C18H18N2Os. Formed by heating (5g of) methyl furfuramide (v METHYL FURFURALDEHYDE) with NaOH (25g) dissolved in water (25 cc) at 100° (Bieler a Tollens, A 258, 123) Oil, which solidifies as an amorphous resin -*B'HNO, lustrous crys-

tals —B'H₂SO, minute needles —B'.H.PtCl. yellow crystalline pp METHYL-FURFUROL v METHYL FURFUR-

ALDEHYDE

METHYL-FURFURYL-ACETIC ACID (?)

CH CMe C₂H₈O₂ 2 e

CH CCH, CO,H CMe CH >co Sylvane-acetic acid

CH, CH CO,H Formed by heating its carboxylic acid (Polonowsky, A 246, 14) Prisms (from water), v e sol alcohol, m sol ether, almost insol cold water Somewhat volatile with steam It gives no colouration with FeCl3, and is dissolved without alteration by conc H SO, Nitric acid oxidises it, yielding acetic and oxalic acids -AgA' aq. bulky white pp - BaA'2 4 2 aq transparent plates or spherical aggregates

Methyl-carboxy-furfuryl-acetic acid (?)

CMe COHC C₈H₈O₅ i e Sylva**ns** CH C CH, CO,H

carboxyacetic acid [207°] Formed, together with methyl furfuryl-carbinyl methyl ketone carboxvlic ether and a neutral substance C14H15O4 [139°], by adding a conc solution of ZnCl. to a mixture of glyoxal and aceto acetic ether in the cold (Polonowsky, A 246, 1) Needles (from hot water), v sol alcohol - (NH₄)₂A" ½aq minute needles —BaA" 2aq transparent needles -Ag₂A''aq

Mono methyl ether MeHA" [980]:

needles -AgMeA

Di methyl ether Me,A" Mono ethyl ether EtHA" [76°]

METHYL-FÜRFURYL-CARBINYL METHYL KETONE DI CARBOXYLIC ACID Ethyl CO Et C CMe

ether CH C CH(CO Et) CO CH,

295°) One of the products formed by the con densation of aceto acetic ether (2 mol) with glyoxal (1 mol) in presence of aqueous ZnCl2 (Polonowsky, A 24b, 18) Light yellow oil, miscible with alcohol, ether, benzene, and chloroform Insol water and alkalis, resimfied by warming with cone H2SO

DI METHYL - FURFURYL KETONE CARBOXYLIC ACID C.H10O4 16. CMe C CO CH₃

OCMe C CO.H Acetyl di methyl furfurans

carboxylic acid [152°] Formed by heating at 225° in a sealed tube a mixture of \$\beta\$ acetyl propionic acid (3g) with Ac₂O (15g), the product being freed from Ac O by distillation in vacua. and the residue extracted with water (Magnanini, B 21, 1523) Small needles (from hot water) --- AgA' crystalline pp, sl sol water -BaA' aq crystalline pp
DI - METHYL GENTISIC ALDEHYDE v.

Di methyl derivative of Di oxy benzoic alde-HYDE

METHYL GLUTACONIC ACID C.H.O. 18 CH, CH(CO,H) CH CH CO,H [187°] Formed by boiling methyl-dicarboxy-glutaconic ether (vol 1 p 706) with cone alcoholic potash (Conrad a Guthzeit, A 222, 259) Nodules (from water), v sol water, alcohol, and ether

a-METHYL GLUTARIC ACID C.H10Q4 26. CO₂H CHMe CH₂.CH₂CO₂H Butane dicarb-[77°] HF 238,200 oxylic acid Mol w 146 HCp 670,800 (Stohmann, HCv 670,500 Kleber a Langbein, J pr [2] 40, 214) by saponifying with cone alcoholic KOH the product of the action of β iodo propionic ether on sodium methyl acetacetic ether (Wislicenus a Limpach, A 192, 133) Formed also by the action of HI and P on γ oxy α methyl glutaric acid (Krekeler, B 19, 3270), and on saccharonic acid CO,H CMe(OH) CH(OH) CH(OH) CO,H a product of the decomposition of glucose (Kılıanı, A 218, 369) Obtained by boiling γ cyano valerio acid $(q \ v)$ with aqueous NaOH (Wislicenus, A 233, 101) Prisms, v sol water, alcohol, and The zinc salt is a viscid mass - Ag_2A''

boiling at 134° (Krekeler, B 19, 3270) Salts $-Ag_*A'' - CaA'' - PbA'' \frac{1}{2}aq$ Trimetric needles $a\ b\ c = 6331\ 1 \ 6072$

Anhydride C₈H₈O₃ [46°] (282°-284°) V 4 61 (calc 4 43) Mass of slender prisms (trom CS₂) V sl sol cold water, neutral to litmus, on boiling it dissolves, becoming strongly acid, changing to the hydrated acid V sol alcohol, ether, benzene, chloroform, or glacial acetic acid, v sl sol petroleum

s D1 methyl glutaric acid C7H12O4 1 e CO₂H CHMe $\overrightarrow{CH_2}$ CHMe CO₂H [114°] (Z), [c 90°] (D), [101°] (B), [106°] (A a J) Formed by treating a cyano-propionic ether with methylene iodide and alcoholic NaOEt, heating the mixture on the water bath, and saponifying the product with HCl (Zelinsky, B 22, 2823) Formed also by heating pentane tetracarboxylic acid either by itself, or in aqueous solution, or by heating its ether with H₂SO₄ (Dressel, A 256, Obtained from sodium methyl malonic ether and methylene iodide (Bischoff, B 23, 1464, 1951) Crystals resembling those of di methylsuccinic acid, v sol water, alcohol, and ether Not volatile with steam According to Zelinsky the product obtained by his method really con sisted of two isomeric modifications, melting at 102°-104° and 128° respectively A solution of the ammonium salt gives white pps with AgNO, and HgCl2, and a brown pp with FeCl2 -Ag2A"

Anhydride OH₂ CHMe CO O [93°]
Formed by boiling the acid for five minutes or by warming it with AcCl (Auwers a Jackson, B 23, 1611) Rectangular prisms (from hot

hgroïn)

Tri methyl-glutaric acid C₂H₁₄O₄ : c CO₂H₂CM₂CH₂CHMe CO₂H. [97°] S 2 2 at

11° Formed, together with the isomeric tetramethyl-succinic and, by the action of finely divided silver one brome isobutyric and (Hell a Wittekind, B 7, 320, Auwers a V Meyer, B. 23, 300) Flat plates (from hot water), sol cold water, m sol CS₂ and ligroin, v sol other solvents Can be distilled in small quantities Not volatile with steam When the acid (6 g) is mixed in the cold with dry red phosphorus (8 g) and bromine (16 g) the product is brome trimethyl glutaric anhydride (114°)

methyl glutaric anhydride [114°]

Anhydride CH₂ CHMe CO [96°]

(262°) Formed by boiling the acid for some time, or by heating it with excess of Ac₂O Coarse flat setum needles (from hot lurgur)

Coarse flat satiny needles (from hot ligroin)

Ethyl ether Et₂A'' (230°) S G º 1 012

METHYL-GLYCERAMINE $C_4H_{11}NO_2$ is $CH_{2}(OH)$ CH(OH) CH₂NMeH Formed, together with the following body, by heating the (a) chlorhydrin of glycerin with aqueous NMe₃ in sealed tubes at 100° (Hanriot, A. Ch. [5] 17, 62, of vol in p. 623)

Tri-methyl-glyceramine chloride
CH₂(OH) CH(OH) CH₂NMe₂Cl Formed by heating glycerin chlorhydrin with trimethyl amine on the water bath for 12 hours (Hanriot, C R 86, 1335)—C₃H₂O₂NMe₃Cl syrup—(C₃H₂O₂NMe₃Cl)₂FtCl₄ orange tables, sol water, insol alcohol, not decomposed by boiling the aqueous solution

DI-METHYL-GLYCERIC ACID v DI OXY

a METHYL-GLYCIDIC ACID C₁H₀O₃ re
CH₂
Propylene oxule carboxylic
CMe CO,H

acid Formed by decomposing chloro oxy iso butyric acid (the product of the union of HOCl with methacrylic acid) with alcoholic potash (Mélikoff, Bl [2] 41, 311, 43, 115) Thick liquid, \mathbf{v} sol water and ether

Reactions—1 When heated with water for half an hour it forms di oxy butyric acid CH₃ CH(OH) CH(OH) CO₂H [100°]—2 Heated with ammonia it forms oxy amido isobutyric acid—3 Conc HCl combines, forming chloro oxy isobutyric acid [107°]—4 HBr forms bromo oxy iso butyric acid [101°]

Salts—KA' ½aq glittering plates, sl sol cold alcohol—AgA' thin needles (from hot water)

E'thyl ether EtA' (164°) SG 15 1 0546 From AgA' and EtI (Mélikoff, B 21, 2053) Oil .CHMe

β Methyl-glycidic acid O | [84°] CH CO₂H Formed by the action of alcoholic potash on

Formed by the action of alcoholic potash on chloro oxy butyric acid (63°) (the product of the union of HOCl with crotonic acid) (Mélikoff, Bl [2] 43, 115) Trimetric crystals (from ether), ve sol water, m sol ether Volatile with steam

Reactions —1 Combines with HCl forming chloro oxy butyric acid [86°]—2 HBr yields bromo oxy butyric acid [90°]—3 Ammonia forms oxy amido butyric acid —4 When heated with water it slowly combines, forming di oxybutyric acid [80°]

Salts—KA' aq powder, v sol water, si. sol cold alcohol—AgA'. crystalline powder

Ethylether EtA' (174°) SG $\frac{15}{15}$ 1 0534 (Mélikoff a Zelinsky, B 21, 2052)

as Di-methyl-glycidic soid C₂H₂O₃ is CHMe OH₂ OH₂ [62°]

CMe CO₂H OH CHMe CO₂H Formed by the action of alcoholic potash on chloro oxy valeric acid (the product of the union of HOCl on angelic acid) [45°] (Melikoff, Bi [2] 47, 166, A 257, 118) Minute prisms, v sol water, alcohol, and ether Unites with HCl, forming chloro oxy valeric acid [75°] Water at 99° converts it into di oxy valeric acid [107°]

Salts $-KA' \frac{1}{2}$ aq prisms -AgA' th

Ethylether EtA' (178°) S G 15 1 0250 From AgA' and FtI Oil

METHYL-GLYCOLLIC ACID v Methyl deri vative of Glycollic acid

DI-METHYL-GLYCOLURILE v DI METHYL

Tetra-methyl glycolurile v Glyoxal, Reac tion 13

METHYL-GLYOXAL v PYRUVIC ALDEHYDE DI-METHYL-GLYOXAL v DI METHYL DIKE

METHYL-GLYOXALINE $C_4H_6N_2$ \imath e

methyline Methyl imidazole $[-6^{\circ}]$ (198°) S G $\stackrel{10}{\cdot}$ 1 0363

Formation —1 By the action of sodium amalgam on tri bromo methyl glyoxaline (q v) m alcoholic solution (Wyss, B 10, 1372) —2 By methylation of glyoxaline (Wallach, B 15, 644, A 214, 319) —3 From sulphydro methyl glyox

aline HS C | NMe CH | by treatment with dilute

nitric acid (Wohl a Marckwald, B 22, 1359) — 4 By reducing chloro methyl glyoxaline with HIAq and P at 140° (Wallach, A 214, 310)

Froperties —Liquid, sol water With aque ous HgCy. it gives a pp composed of slender needles [119°] Combines readily with MeI, forming a methylo iodide, whence B'Me₂PtCl₈ [206°] may be obtained

Salts—B'.H PtCl₆ [191°] S 44 at 13° (W) 75°5 at 13° (W a M) Orange red prisms—B'.H ZnCl₄ [128°-131°] Soluble crystals—B'HNO₃ Prisms—B'C₆H (NO₂)₃OH. [158°] Needles, sl sol alcohol and ether—B'HAuCl₄ [120°]

Methyl glyoxaline CMe | Glyoxal-

sthyline Para oxalmethyline [137°] (267°) Formation -1 By saturating an aqueous solution of glyoxal (1 mol) and acetic aldehyde (1 mol) with ammonia (Radziszewsky, B 15, 2706, 16, 487) -2 By passing the preceding methyl glyoxaline [-6°] through a red hot tube (Wallach, B 16, 541) -3 By distilling the zinc salt of the preceding methyl glyoxaline or of chloro methyl ethyl glyoxaline with lime (Wallach, A 214, 296)

Properties —Long thin needles, v sol water, alcohol, and hot benzene, m sol cold benzene Decolourises bromine, forming C.H.Br.N. [258°] Yields oxamide on oxidation with H.O. (Radzi-

SG $\frac{15}{15}$ 1 0534 | szewsky, B 17, 1290) Its solutions are ppd by tannin and by pieric acid.

Salt $-B'H_2PtCl_s$ Trimetric needles D1-methyl-glyoxaline $C_sH_sN_2$ i θ

NMe CH

OMe

N — CH

Oxalmethylethyline (206°).

S G 11 10051 Formed by the action of MeI on methyl-glyoxaline (Radziszewsky, B 16, 488). Liquid with narcotic odour, sol water, alcohol, and ether Its solution gives with CuSO₄ a blue pp, with AgNO₂ a crystalline pp, with HgCl₂ with tannin, and with phosphomolybdic acid white pps, and with picric acid a yellow pp All these pps are soluble in hot water—
*B'_H_PtCl₄ [138°]

Methylo iodide B'MeI Crystalline

Chloro di methyl - glyoxaline C₃H,ClN₄. (213°) Formed by the action of PCl₃ on methylethyl oxamide (Wallach, A 184, 71) — B'HOL Prisms—B'₂H,PtCl₆—B'₂AgNO₃—B'MeL Tri-methyl-glyoxaline C₆H₁₆N₂ 1 e

Tri-methyl-glyoxaline C, H₁₀N₂ t e

N CMe

NH CMe

Or CMe

N CMe

(271°) Formed by adding di methyl diketone CH₁ CO CO CH₂ to an ammoniacal solution of AgNO₃, and decomposing the resulting pp with dilute HCl (Fittig, A 249, 206) Formed also, with other bases, by heating di methyl diketone with cone NH₃Aq at 100° for an hour (Von Pechmann, B 21, 1411) Small white needles (from ether or ligroin) Not affected by nitrous acid—B'HCl tufts of snow white needles

METHYL-GLYOXIM v Oxim of Pyruvic ALDEHYDE

Di methyl glyoxim v Di Acetyl and Di METHYL DIRFTONE

DI-METHYL-GLYOXYL-UREA C₃H₈N₁O₃ t 6

NMe CH(OH)

CO

Formed by reducing cho-

NMe CO

lestrophane CO | NMe CO | In aqueous solution

with zinc and H SO, (Andreasch, M 3, 436) Small needles, melting below 100° May be sublimed V e sol water and alcohol, insolether Decomposed by boiling baryta water into CO, methylamine, and glyoxylic acid Readily re oxidised to cholestrophane

METHYL GUANACIL v GUANIDINE, Reaction 11

METHYL-GUANAMINE The name originally given by Nencki to Acetoguanamine, vol. 11 p. 655

11 p 655

METHYL-DIGUANIDE $C_1H_2N_3$ Obtained, in combination with CuSO₄, by adding a 20 p c solution of methylamine to a mixture of di-oyan di amide $C_2N_2(NH_2)$, and copper sulphate, the crystalline $(C_3H_4N_5)$, CuSO₄ $2\frac{1}{2}$ aq which separates is then decomposed by baryta (Reibenschuh, M 4, 388) Thick alkaline syrup, which absorbs CO_2 from the air

Safts — Colourless leaflets or prisms, v sol. water — B'₂H₂SO₄ Prisms, obtained by decomposing B'₂CuSO₄ by H₂S — B'H₂SO₄ From B'₂H₃SO₄ and H₂SO₄ Crystalline powder V al sol alcohol — Cu(C₂H₂N₃)₂ 3\$aq Formed by shaking di cyan diamide with cupric oxide and methylamine Rose-red crystalline powder —

B',CuSO, 2 ag Pink needles — The chromate and piciate form yellow prisms

METHYL-GUANIDINE $C_2H_7N_3$ re

NH C(NH₂)(NHMe) Methyl uramine Formation—1 By boiling an aqueous solu tion of creatine with HgO or with PbO₂ and dilute H₂SO₄ (Dessaignes, C R 38, 839, 41, 1258, A 92, 407, 97, 340) —2 By oxidising crea tinin with KMnO, (Neubauer, A 119, 46) -3 By heating cyanamide with methylamine hydro chloride in alcoholic solution at 100° (Erlenmeyer, B 3, 896) -4 By the action of methyl cyan. amide on NH₄Cl (Tavildaroff, B 5, 477)

Properties — Strongly alkaline, deliquescent, crystalline mass Decomposed by KOH, giving off NH3 and methylamine When boiled with chloro acetic acid it yields glycolyl methylguanidine C4H11N3O8, which crystallises in tablets, v e sol water, and neutral in reaction, and forms the salts C4H11NO23HCl, and

C4H11N8O8H2PtOL

Salts — B'_HPtCl_s Monoclinic crystals (Haushofer, J 1878, 351) S 143 at 19° — B'HAuCl₄ Trimetric crystals, v sol ether, m Monoclinic crystals B'HAuCl₄ Trimetric crystals, v sol emer, in sol water —B₁H₂C₂O₄2aq Crystals, v sol water Di-methyl-guanidine C₃H₅N₃ v e

NH C(NH2)(NMe) Formed by heating equimolecular quantities of cyanamide and dimethylamine hydrochloride at 110° (Tartarinoff, C R 89,608)

-B'HCl Trimetric crystals, a b c Salts . = 862.1 x (Haushofer, Z K 6,130) — $B'_2H_2PtCl_6$ Triclinic crystals, a b c = 941 1 678, a = 90° 55′, β = 90° 20′, γ = 90° 4′—B′HAuCl, Trimetric crystals (Haushofer, J 1882, 364)

s - Di - methyl - guanidine NH C(NHMe), Formed by the action of methylamine on cyanogen iodide (Erlenmeyer, B 14, 1868)

Platinochloride B.H.PtCl₆ Triclinic crystals, $a \ b \ c = 1 \ 212 \ 1 \ 1 \ 761$, $a = 90^{\circ} \ 22'$, $\beta = 110^{\circ} \ 20'$, $\gamma = 90^{\circ} \ 5'$ METHYL - GUANIDO - ACETIC ACID v

(a) METHYL-GUANIDO-BENZOIC ACID $C_9H_{11}N_3O_2$ 1 e NH $C(NH_2)$ NMe C_6H_4 CO NH C(NH₂) NMe C₆H₄ CO₂H (a)-Benzcreatin Formed by methylation of benzglycocyamine (Griess, B 8, 324) Small acccular plates (containing 11 aq), sl sol hot water and alcohol Decomposed by boiling baryta water into methyl amido benzoic acid and urea —HA'HClaq plates, m sol water — (HA')2H2PtCl62aq

Anhydride v Benzcreatinine

(β)-Methyl-guanido-benzoic acid $C_9H_{11}N_2O_2$ * NH C(NHMe) NH C6H4 CO2H Formed by the action of a cold concentrated solution of methyl amine on the so called ethoxy carbimidamido benzoic acid (Griess, B 8, 325, vol 1 p 157) Plates, sl sol cold water and alcohol Decom posed by baryta-water into mamido benzoic acid, CO₂, and methylamine — HA'HCl — (HA')2H2PtCl2aq

Anhydridev (β) Benzcreatinine METHYL-GUANIDO-ETHANE SULPHONIC ACID CN₄H₂Me(CH₂ CH₂ SO₂H) or probably NH C(NHMe)NH CH₂ CH₂ SO₂H Formed by heating methyl amido ethane sulphonic acid (2 grms) and cyanamide (7 grms) with enough water to dissolve them, for 5 hours at 120° Crystals of the new body are found in the tube (E. Dittrich, J. pr. [2] 18, 72). Transparent

monoclinic prisms Crystallises with a molecule of water that goes off at 110° V sol hot, m sol cold, water, insol alcohol and ether Turns brown at 285°, giving off methylamine Does not form salts

METHYL-GUANIDO-VALERIC ACID

hydride C,H, N,O ie

(CH_s)₂CH CH $\stackrel{NMe}{<_{CO\ NH}}$ C NH Isovalercrea-Formed by heating methyl - amidoisovaleric acid with cyanamide and ammonia (Duvillier, Bl [2] 39,539) Sol alcohol

METHYL-HEMIPIC ACID v Methyl ether of Hemipic acid

METHYL HENDECYL KETONE C13H26O 2 e. CH, CO C, H., Methyl undecyl ketone [28°] (263°) S G (liquid) 28 823 Formed by distilling a mixture of barium laurate and barium acetate (Krafft, B 12, 1667, 15, 1724) acetic and hendecoic acids on oxidation

Isomeride C₁₃H₂₆O (265°-275°) S G 15 887 One of the products of the action of CO on a mixture of NaOAc and NaOC₅H₁₁ at 180°

(Poetsch, A 218, 62) Liquid

METHYL HEPTADECYL KETONE C, H, SO ie CH₃ CO $C_{17}H_{35}$ [56°] (267° at 110 mm) S G (liquid) $\frac{59}{2}$ 811 Prepared by distilling a mixture of barium stearate and barium acetate On oxidation it gives margaric acid (Krafft, B 12, 1672, 15, 1724)

Methyl heptadecyl ketone C19H38O 2 c CH, CO CH(C₈H₁₇)₂ Dr octyl acetone (325°-330°) Formed by boiling di octyl acetoacetic ether with alcoholic potash (Guthzeit, A 204,

METĤYL HEPTINYL KETONE C,H,,O i e CH, CO CH(C,H)₂ Dr allyl acetone (175°) Formed by boiling di allyl acetoacetic ether with cone KOHAq (Wolff, A 201, 48) V sol alco hol and ether

METHYL HEPTINYL OXIDE C8H14O 1 e CH₃ O CH(C₃H₅)₂ (136°) S G $\frac{6}{0}$ 8258 Formed from NaOCH(C₃H₅), and MeI (Rasbinin, J pr [2] 23, 270) Yields, on oxidation by cold KMnO,

CH₂O CH(CH₂ CO₂H),

METHYL HEPTYL KETONE C₂H₁₈O 16 CH₃ CO CHPr₂ Dr propyl - acetone (174°)Formed by heating di propyl acetoacetic ether with alcoholic potash (Burton, Am 3, 390) Liquid Appears not to combine with NaHSO,

Methyl heptyl ketone CH₃ CO C₇H₁₅ (177°) Formed by the decomposition of sec hexyl acetoacetic ether by KOH (Lundahl, B 16,789)

METHYL HEPTYL OXIDE C₈H₁₈O 2e CH₈ O C₇H₁₈ (161°) S G 165 830 V D 4 2 (calc 4 5) S V 194 6 (Lossen, A 254, 57) (calc 45) SV 1946 (Lossen, A 254, 57) Formed by the action of MeI on NaOCH derived from cenanthol (Wills, C J 6, 314) Mobile liquid, with strong odour, insol water, v sol alcohol and ether

METHYL-HESPERETIC ACID v Dimethyl derivative of CAFFEIC ACID

METHYL-HEXADECYL-BENZENE v HEXA-DECYL-TOLUENE

Di-methyl-hexadecyl-benzene v HEXADECYL-

Tri-methyl-hexadecyl-benzene v Hexadecyl-MESITYLENE

METHYL-HEXANE v HEPTANE. METHYL-HEXOSE C,H14O, 20 CH. CH(OH) CH(OH) CH(OH) CH(OH) CH(OH) CHO 181°] Formed by reducing the lactone of rhamnose carboxylic acid with sodium amalgam (Emil Fischer, B 23, 936) Crystallises from methyl alcohol Hydrogen cyanide yields C₈H₁₈O₆N, which on saponification forms methyl heptonic acid C₈H₁₆O₈, the lactone of which crystallises easily, and gives rise, on reduction, to methyl-heptose $CH_3(CH\ OH)_3$ CHO, of which the phenyl hydrazide is sl sol water

V sol water Phenyl-hydrazide [200° with decomposition] Osazone METHYL HEXYL-CARBINOL v

DI METHYL HEXYLENE DIKETONE

C₁₀H₁₈O₂ ie (CH₃CO),CH C₅H₁₁ Iso amyl acetyl acetone (c 222°) Formed by heating (CH₃ CO)₂CHNa with isoamyl iodide at 180⁵ (Combes, A Ch [6] 12, 249) Liquid Decom posed by caustic potash into acetic acid and

CH₂ CO CH₂ C₃H₁₁
D₁ methyl hexylene C10H18O2 diketone CH₃ CO CH₂ CH₂ CH₂ CH₂ CHMe CO CH₃ a methyl ac-di acetyl pentane $(232^{\circ}-235^{\circ})$ Formed by decomposing its carboxylic ether with alcoholic potash (Kipping a Perkin, C J 55, 346) Colourless mobile oil Dissolves in a solution of NaHSO, and is reprecipitated by

K₂CO, DI METHYL HEXYLENE DIKETONE

CARBOXYLIC ETHER C13H22O4 1 e CH, CO CMe(CO2Et) CH2 CH2 CH CH2 CH2 CH2 (255°-260°) Formed by the action of NaOEt and BrCH₂ CH CH₂ CH₂ CO CH₃ on methyl acetoacetic ether (hipping a Perkin, C J 55, Colourless liquid, with faint odour, v sl sol water

METHYL-HEXYL-GLYOXALINE C10H18N2

NMe CH (262°) SG 165 928

Formed by heating hexyl glyoxaline with a solution of MeI in methyl alcohol (Karcz, M 8, 221) Colourless oil, insol water, sol alcohol and ether Gives the alkaloidal reactions -B'2H.PtCl6 yellow plates, sol water

Methylo rodide B'MeI [124°] V sol

alcohol and ether

METHYL n HEXYL KETONE C.H. O 1.6 CH₃ CO CH₂ CH₂ CH₂ CH₂ CH₃ (172°) S G ²⁹ 8185 (Bruhl, A 203, 29), $\frac{9}{2}$ 835 (C) 186 6 (R Schiff, A 220, 103) $\mu_{\beta} =$ $\mu_{\beta}=1\ 4213$ R_∞ 63 29 H C 1,209,510 (Louguinine, Bl [2] 41, 389)

Formation —1 By distilling sodium ricinoleate with NaOH (Limpricht, A 93, 242, Bouis, A 97, 34) -2 By distilling a mixture of calcium acetate and calcium n heptoate (cenanthate) (Stadeler, J pr 72, 246) -3 From octoic aldehyde by treatment with PCl, decomposing the resulting C₁H₁₃CHCl₂ by alcoholic KOH, and adding the octinene C₆H₁₃ C CH so formed to cold H2SO4, diluting and distilling with water (Béhal, Bl [2] 47, 33, A Ch [6] 15, 275) -Together with ethyl amyl ketons by treating C.H., C C CH, with H.SO, and water successively (Béhal, Bl [2] 48, 704) —5 'Oil of wine' contains a methyl hexyl ketone (164°), which yields hexore and acetic acids on oxidation (Hartwig, Scholl, J pr. [2] 23, 449) -6 By heating octyl alcohol with boracic acid at 170°, and distilling en pacuo (Councler, B 11, 1108)

Properties - Colourless, mobile liquid, smell ing like apples and tasting like camphor, sol alcohol and ether, insol water Combines with NaHSO₃, forming a compound sol alcohol, but decomposed by hot water Does not reduce ammoniacal AgNO, or Fehling's solution Chromic acid mixture oxidises it to acetic and hexoic acids (Béhal a Combes) Nitric acid oxidises it to heptoic acid (Petersen, A 118, 78) PCl, forms C₈H₁₆Cl₂ (190°-200°) (Dachauer, A 106, 271) Combinations — C₈H₁₆OKHSO₃ 3aq — C₈H₁₆ONH₄HSO₃ V sol water (L) Oxim CH₂ C(NOH) C₈H₁₅ (214°) at 725 mm (B 21, 509, c f Béhal, Bl (2) 47, 163)

Methyl isohexyl ketone CH₃ CO CH₂ C₅H₁₁ Isoamyl acetone (170°) Formed by the action of KOH upon di methyl hexylene, diketone $(CH_3 CO)_2 CH C_3 H_{11} (Combes, A Ch [6] 12, 249)$ Limpid liquid, with agreeable odour with NaHSO,

Methyl hexyl ketone (?) Me CO C₆H₁₃ (208°-210° cor) S G 15 843 Occurs in small quan tity (40 g) among the products of the passage of CO over a mixture of sodic acetate (546 g) and sodic iso amylate (746 g) (Poetsch, A 218, 60) Methyl hexyl diketone $C_8H_{14}O_2$ i.e

CH₃ CO CO CH₂ CH₂Pr (165°) (Von Pechmann, B 21, 2140)

DI-METHYL-HEXYL-PYRIDINE $C_{1}H_{2}N$

 C_bH_{13} C < CH CMe > Nn Hexyl lutidine (250°) at 719 mm Obtained by distilling its dicarboxylic acid with lime (Jaeckle, A 246, 41)

Colourless liquid, with faint blue fluorescence B'2H.PtCl, [163°] Orange prisms -B'2AgNO, White needles, sol hot water and alcohol

Hexahydride C, H. N 26 C.H. CH CH NH Hexyl lupetidine

Obtained by the action of (240°) at 715 mm sodium amalgam on an alcoholic solution of di methyl hexyl pyridine (J) Colourless oil, not exhibiting fluorescence Its dilute alcoholic solu tion gives a dark brown pp, with mercurous nitrate Its platinochloride and dichromate could not be obtained in a crystalline state-B'HCl long white prisms, v sl sol water

DI-METHYL-HEXYL-PYRIDINE DICARB. OXYLIC ACID C15H 1NO. 1e

C_cH_{1s} C C(CO₂H) CMe N Hexyl lutidine ds-carboxylic acid The potassium salt is formed by saponifying its ether with boiling KOHAq (Jackle, A 246, 40) The free acid has not been prepared -PbA" 13aq

Dr ethyl ether Et,A" Formed by oxidising its dihydride with nitrous acid Yellowish. brown oil, forming salts with mineral acids -H₂A"H₂PtCl₈ [141°] Orange plates

Dihydride De ethyl ether

 $C_{e}H_{1s}CH < C(CO_{e}Et)CMe > NH$ [54°] Formed by the condensation of heptoic aldehyde (cenanthol) (1 mol) with acetoacetic ether (2 mols) and ammonia (1 mol) (J) Yellow prisms, crystallising with difficulty from a dilute alcoholic solution

DI-METHYL-HOMO-CAFFEIC ACID v Damethyl derivative of (4 3.1) DI OXY-PHENYL-CRO-TONIC ACID.

METHYL-HOMO FERULIC ACID v Dimethyl derivative of (4 3 1) Di-OXY PHENYL-CROTONIC ACID

METHYL-HYDANTOIC ACID C₄H₈N₂O₂ re NH₂ CO NMe CH₂ CO₂H Methyl uramido acetic acid

Formation—1 Occurs in the urine of a dog whose food is mixed with methyl amido acetic acid (Schultzen, B 5, 578)—2 By digesting an aqueous solution of sarcosine with potassium cyanate and ammonium sulphate for two days at 40° (Baumann a Hoppe Seyler, B 7, 35)—3 By boiling methyl amido acetic acid with ursa and excess of baryta-water, or by digesting the same mixture for two days at 40° (B a H)—4 By the action of potassium cyanate and H₂SO₄ on methyl amido acetic acid (E Salkowsky, B 7, 116)

Salkowsky, B 7, 116)

Properties—Transparent plates (from alcohol), m sol cold water and cold alcohol, v sol hot water and hot alcohol Acid in reaction When the concentrated aqueous solution is boiled it is partially converted into methylhydantoin, this dehydration is more rapidly deffected by boiling with water and PbCO₃ or BaCO₃, only traces of the acid then passing into solution. When heated in a sealed tube with a saturated solution of baryta at 140° it yields NH₃, methyl amido acetic acid, and CO₂. Moist Ag₂O forms lamine of silver methyl hydantoin

Salts — *BaA'₂ Ppd by adding alcohol to its aqueous solution — *CuA'₂ Amorphous

Di methyl hydantoic acid v Acetonuramic

METHYL - HYDANTOIN $C_1H_eN_2O_2$ • 6 $CO < NMe CH_2 > Anhydrade$ of methyl ura mudo acetic acid Mol w 114 [182°] (F a K), [156°] (E Salkowsky, B 7, 119), [145°] (N)

Formation—1 By heating creatinin with baryta water at 100° in a sealed tube (Neubauer, A 137, 288)—2 By boiling methyl hydantoic acid with water and PbCO₂ or BaCO₂—3 By melting methyl-amido acetic acid with urea (Huppert, B 6, 1278)—4 By the action of cyanogen chloride on melted methyl amido-acetic acid (Traube, B 15, 2110)—5 By warming caffuric acid with baryta water (Fischer, A 215, 286)—6 By the reduction of methyl allantoin by HI (Hill, B 9, 1091)—7 By heating a mixture of hydantoin (3 pts), MeI (6 pts), methyl alcohol (16 pts), and KOH (2 pts), for three hours at 100°, and extracting the product with boiling alcohol (Franchimont a Klobbie, R T C 8, 289)

Properties —Short prisms, v sol boiling water, sl sol cold water, v sol alcohol, v sl sol ether May be sublimed It does not unite with baryta, but its hot solution dissolves Ag₂O, and the alkaline filtrate then deposits C₄H₃AgN₂O₂ as groups of thin lamine. The mercuric compound, obtained in like manner, forms nodular groups of minute needles, very soluble in water Nitric acid (S G. 15) converts methyl hydantom into the nitramine

 $\rm CO < NMe-CH, \ \)$ which crystallises from alcohol in scales [168°], v sl sol cold water, de composed by bolling water

(a)-Methyl-hydantoin v Lactyl-URBA.

Di-methyl hydantoïn C₃H_aN₂O₂ s.e NH CMe₂

METHYL-HYDANTOIN CARBOXYLIC ACID C₃H₆N₂O₄ Formed by boiling caffuric acid with baryta water (E. Fischer, A. 215, 286). The free acid is decomposed into CO₂ and methylhydantoin when its aqueous solution is warmed

[156°] Formed, together with hydrastine methylo hydroxide, by the action of alkalis on a solution of hydrastine methylo chloride pared by adding potash to a hot aqueous solution of hydrastine methylo iodide until no further ppn takes place (Freund a Rosenberg, B 23, 406) Small yellow needles (from alcohol), almost insol water, sol chloroform, benzene, CS, ether, and dilute alcohol With sulphomolybdic acid (Frohde's reagent) it gives a violet colour, changing through blue to green Forms spa ringly soluble double salts with SnCl, And chloride, and HgCl, Ammonia converts it into the amide $C_{22}H_{26}N_2\tilde{O}_6$ [180°] which forms a crys talline hydrochloride C 2H26N2O6HCl 2aq, and on boiling with dilute nitric acid yields hemipic acid (Freund a Heim, B 23, 2902) The formula of this amide may be written

C,H2(OMe2)CONH2

CO CH₂ C₆H₂(O₂GH₂) CH₂ CH₂NMe₂

and it may also be got by heating hydrastine methylo iodide with alcoholic ammonia. The corresponding methylamide $C_{22}H_{-8}N_2O_6$ [182°], ethylamide $C_{24}H_{56}N_2O_6$ [162°], allylamide $C_{22}H_{36}N_2O_6$ [158°], and amylamide $C_{27}H_{36}N_2O_6$ [171°] have been prepared

Salts—B'HCl [241°] M sol hot water Decomposed on fusion A 1 p c solution is in active—B'₂H₂PtCl₈ sl sol water—B'H SO₄ [250°] Less soluble than the chloride—B'HNO₃ Decomposes at 250° V sl sol water

Methylo-rodrde C₂₂H₂₂NO₅MeI Yellow needles, more soluble in water than in alcohol Decomposes at 250° On warming with aqueous KOH it gives off trimethylamine

Methyl-hydrastimide C22H21N2O5 s.e

C₀H_{*}(OMe), CONH C₀H_{*}(O₄OH_{*}) CH_{*} CH_{*} NMe_{*} [192°] Formed by the action of dilute H_{*}SO₄ on the amide (Freund a Heim, B 23, 2899) Yellow needles, insol water, sl sol alcohol—B'HCl [227°]—B'HCl xaq.—B'₂H_{*}PtCl_{*} [205°].

-B'H.SO. [218°] Yellow crystals (from alcohol) -B'HNO, aq

Methylo-rodide B'Mel ag

Methyl hydrasteineC₂₂H₂₇NO₈ [151°] Formed by warming hydrastine methylo-chloride with excess of KOHAq, or, better, by warming methyl-hydrastine with strong caustic potash (Freund a Rosenberg, B 23, 408) Colourless needles (containing aq) (from water), sl sol cold water, more sol hot water and alcohol Decomposed by long heating at 110° Very soluble in alkalis, but reppd by CO2, insoluble in aqueous Na2CO3 It dissolves in aqueous NH₃, but is ppd on eva poration It also dissolves in HClAq In a 5 pc hydrochloric acid solution it is inactive Tertiary base Coloured reddish brown by chlorine water and ammonia Iouine has no Hot conc HBrAq reconverts it into methyl hydrastine Its salts are colourless -B'HCl aq [290°] Compact groups of crystals

Methyl hydrastinine Methylo rodide C₁₃H₁₈NO₂I i e CHO C₇H₄O₂ CH₂ CH₂ NMe₂I [267°] Formed by heating hydrastinine with Pale yellow needles MeI (Freund, B 22, 2329) (from alcohol or water) AgCl gives C13H18NO3Cl [213°], which forms white crystals (containing aq) -(C₁₃H₁₈NO₈Cl)₂PtCl₄ yellow crystalline pp

Oxim of the methylo rodide HON CH C9H,O. NMe3I Yellowish needles, de composed at 250° V sol alkalıs and ppd un changed by acids Gives a dark reddish brown pp with platinic chloride

METHYL HYDRAZINE CN₂H₆ ie CH₇ NH NH (87° 1 V) at 745 mm Formed by treating methyl uiea nitrate with NaNO, re ducing the resulting nitroso methyl urea [124°] with zinc and dilute acetic acid, and decomposing the product with HCl (Bruning, B 21, 1810, A 253, 7) Mobile liquid with strong ammoniacal odour, soluble in water (heat being evolved), miscible with alcohol and ether Reduces Feh ling s solution

Salts - B'H₂SO₄ [139 5°] White needles v sol water, sl sol alcohol --B'HCl v sol $[162^{\circ}]$ water and alcohol -B'C,H (NO),OH Yellow needles, decomposed on fusion

Di benzoyl derivative CH, N. HBz, [c 143°] Colourless needles (from water), m sol hot water, v sol alcohol, sl sol ether Does

not reduce Fehling's solution

Picryl derivative CH, N2H2C6H2(NO.), [171°] Obtained from the hydrazine and picryl chloride (chloro tri nitro benzene) in diluted al coholic solution Yellow plates, v sol alcohol and ether, m sol chloroform Decomposed on

Oxalyl derivative CH₈N₂H₂ CO CO N₂H₂CH₃ [221 5°] Formed by adding an aqueous solution of methyl hy drazine to oxalic ether White needles, v sol alcohol, m sol water, v sl sol ether Sublimes at about 160° in needles Reduces Fehling's Nitrous acid forms the nitrosamine CH₃ N₂H(NO) CO CO N₂H(NO) CH₃ [147°]

Di methyl-hydrazine $C_2H_4N_2$ i.e NMe₂ NH₄ (63°) at 720 mm S G $\stackrel{11}{\sim}$ 801 V D (H=1) 30 Prepared by reducing di methyl nitros amine (OH₁)₂N NO with zine dust and acetic acid (Fischer, B 9, 111, Renouf, B 13, 2171) Fermed also by reducing di methyl nitramine

(CH₂)₂N NO₂ (Franchimont, R T C 2, 123) Light volatile liquid with ammoniscal odour, v sol water, alcohol, and ether Its haloid salts

volatilise without decomposition

Reactions —1 CS₂ forms di methyl thio-carbazic acid NMe₂ NH CS₂H —2 Phenyl thiocarbimide(phenyl mustard oıl) C.H.NH CS NH NMe2-3 Oxalic ether pro duces NMe2 NH CO CO NH NMe2 -4 Alkul vodides unite, forming azonium iodides, such as NH₂ NMe₃I -5 K₂S₂O, forms NMe₂ NH SO₃K, which crystallises in white plates, v sol water It is split up by hot HClAq into dimethyl hydrazine and H₂SO₄ —6 HgO oxidises it, form ing tetra methyl tetrazone NMe, N N NMe, a yellow oil (130°) which explodes when heated above its boiling point It forms a mirror with ammoniacal AgNO_s, even in the cold, and is de composed by boiling dilute acids into formic aldehyde, NH₂Me, nitrogen, and NHMe₂. The tetrazone is a strong base -7 Nitrous acid de composes it into N₂O and dimethylamine -8 Acetophenone at 100° forms NMe, N CMePh, a hquid (165° at 100 mm) It is split up again by acids into its generators (Reisenegger, B 16,

Salts -B'HCl -B H,Cl, hygroscopic crys tals -B'2H.PtCl, orange yellow prisms, v sol water, sl sol alcohol - B', H, SO, [105°] White needles —B'₂H C O₄ colourless plates, v sol water and alcohol, sl sol ether

Ethylo chloride NH...NMe.EtCl tallises with difficulty, v e sol water ethylo hydroxide is reduced by zinc dust and acetic acid to HCl, ammonia, and NMe.Et -(NH2 NMe EtCl) PtCl. Crystals

DI-METHYL-DI HYDRÖ ANTHRACENE $\,v\,$ DI METHYI ANTHRACENE DI HYDRIDE

METHYL HYDRO-ETHYL PYRIDINE

METHYL FTHYL PYRIDINE HYDRIDE DI METHYL - HYDRO - HOMO - CAFFEÏC ACID v Di methyl derivative of (4 3 1) Di oxi PHENYI ISO BUTYRIC ACID

METHYL-HYDRO HOMO FERULIC ACID vDi methyl derivative of (4 3 1) Di oxy phenyl ISO BUTYRIC ACID

METHYL DI HYDRO PARVOLINE V PENTA METHYL PYRIDINE DIHYDRIDE

METHYL HYDRO-PYRIDINES v METHYL PARIDINE HYDRIDES

METHYL-HYDRO-QUINALDINE v3 4) DI METHYL QUINOLINE TETRA HYDRIDE

METHYL HYDRO-QUINOLINES v METHYL QUINOLINF HYDRIDES

DI-METHYL HYDROQUINONE $D\iota$ methyl derivative of Hydroquinone

METHYL HYDROQUINONE TRI -METHYL AMMONIUM IODIDE vvodide of the di methyl derivative of Di methyl-AMIDO HYDROQUINONE

METHYL HYDRO TOLUQUINONE methyl derivative of Hydrotoluquinone

METHYL HYDROXYLAMINE v Alkyl de rivatives of Hydroxylamine

METHYL HYPOPHOSPHATE Me, P,O, SG. 15 1 109 From MeI and Ag.P.O. (Sanger, A Saponified by water 232, 11)

Methyl-hypophosphate of calcium

MeCaHP₂O₆ 5aq Needles

METHYLIA. A name formerly used for METHYLAMINE.

METHYL-IMESATIN Described as Imide of Methyl-isatin under Isatin

METHYL-IMIDAZOLE A name employed by Wohl and Marckwald (B 22, 1359) to denote the substance usually called METHYL-GLYOXALINE

METHYL - IMIDAZYL MERCAPTAN

SULPHYDRO-METHYL GLYOXALINE

methyl amido methyl thiazole

METHYL-IMIDO-DI-METHYL-THIAZOLE S C(NMe) NMe [96°] Formed by the action CH CMe / of chloro acetone on di methyl urea (Traumann, A 249, 49) White needles (from water), with strong alkaline reaction Is identical with di

METHYL-IMIDO DI (β) NAPHTHYL SUL-PHIDE NMe $<_{C_{10}H_s}^{C_{10}H_s}>S$ [285°] Formed by heating imido di naphthyl sulphide (10 g) with MeI (5g) and MeOH (12cc) for five hours at Formed also by heating di-(\$) naphthylmethyl amine with sulphur (Kym, B 23, 2459) Lemon-yellow plates or needles Gives a blue colour with H2SO4 containing HNO3

METHYL-IMIDO PHENYL NAPHTHYL

SULPHIDE NMe $< \begin{array}{c} C_{10}H_{\bullet} \\ C_{6}H_{\bullet} \end{array}$ N [133°] Formed by heating NH $< \begin{array}{c} C_{10}H_{\bullet} \\ C_{10}H_{\bullet} \end{array}$ N with MeI and MeOH at 150° (Kym, B 23, 2466) Light greenishyellow needles, sl sol hot spirit, v e sol hot benzene

METHYL IMIDO DI PHENYL SULPHIDE $C_{13}H_{11}NS \ i \ e \ S < C_{6}H_{4} > NMe \ [99 \ 3^{\circ}] \ (c \ 363^{\circ})$ Formed by heating imido di phenyl sulphide (thiodiphenylamine) with MeI and MeOH in sealed tubes at 110° (Bernthsen, A 230, 88, B 16, 2899) Long white prisms (from alcohol), insol water, v sol ether, benzene, and hot HOAc Its alcoholic solution is coloured brown by FeCl₃ Nitric acid forms a yellow nitro deri vative which, unlike that of imide di phenyl sulphide, is insol NaOHAq The nitro deriva tive may be reduced to an amido compound which gives a deep bluish green colour with FeCl₂

action of SCl2 dissolved in petroleum on di phenyl methyl amine NMePh₂ (Holzmann, B 21, 2065) Thin yellow scales (from hot benzene alcohol), insol water, sl sol hot alcohol and ether, v sol hot benzene On heating with sopper it yields di phenyl methyl amine

METHYL IMIDO-DI PHENYL SULPHONE $C_{12}H_{11}NSO_2$ is $NMe < C_6H_4 > SO_2$ Formed by the action of KMnO, on methylımıdo dı phenyl sulphide suspended in water (Bernthsen, A 230, 91) Chains of white needles, often slightly reddish (from alcohol) or small compact prisms (from glacial acetic acid) V sl. sol cold alcohol, glacial acetic acid of ether Insol acids or alkalis, not affected by boiling KOH or HCl Boiled with conc H2SO4 it forms a splendid blue liquid, turned pale violet-brown by pouring into water Its nitro-derivative after reduction gives no colour with FeCla.

METHYL INDAZINE C.H.N. t.c.

C,H NH. Quinazole, Methyl indasole. [113°]. (281° 1 V) at 736 mm VD 4 37 (calc 4 53) Formed by slowly adding NaNO₂ to a paste composed of o amido acetophenone and HClAq The resulting diazo compound is soluble in water, and the liquid is poured into a solution of Na,SO₃ The product at first contains CH₃ CO C₆H₄ NH NHSO₃Na, but it gradually loses its reducing power, and deposits needles of

CMe N SO, Na When these needles are

heated with HClAq they yield methyl indazine and H₂SO₄ (Fischer a Tafel, A 227, 303) Methyl indazine is also formed, together with carbonic acid gas, when indazyl acetic acid

CCH, CO,H C₆H₄ is heated

Properties - Colourless needles (from water), m sol hot water, v sol alcohol, ether, and chloroform, almost insol cone NaOHAq be sublimed Does not reduce Fehling's solu Gives crystalline compounds with metallic salts

Salts—B'HCl [177°] Needles, v sol water and alcohol—Sulphate needles— Picrate yellowcrystalline powder -Platino chloride yellow needles

Nitrosamine C.H.N.Oie

N NO [60°] From B'HCl and

cold aqueous NaNO, Yellow needles, v sol. alcohol, ether, and chloroform

Di methyl indazine C₂H₁₀N₂ i e

NMe [80°] Formed by methyla-

tion of the preceding Colourless plates, v sol alcohol, ether, benzene, and hot water

Di methyl ψ indazine $C_6H_4 < \frac{CMe}{NMe} > N$ [36°]

Formed from methyl o amido acctophenone by conversion into the nitrosamine

CH3 CO C6H4 NMe NO and reducing this body with zinc and HOAc (Fischer a Tafel, A 227, 336) Yellow oil, solidifying on cooling as nearly colourless plates Very volatile with steam It forms crystalline compounds with metallic salts -The chloride forms colourless needles -

The sulphate crystallises in needles, and the picrate in rectangular tables

METHYL INDAZINE v-SULPHONIC ACID $C_8H_8N_2SO_2 \quad \text{i.e.} \quad C_8H_4 \begin{matrix} CMe \\ | \\ N- \end{matrix} N \ SO_3H$ The

sodium salt of this acid is formed as described under methyl indazine It is m sol cold water, but ppd on addition of NaOH or NaCl It does not reduce HgO or Fehling's solution Boiling cone HClAq splits it up into NaHSO, and methyl-indazine

METHYL INDAZOLE v METHYL INDAZINE. DI-METHYL-INDIGO v Indigo METHYL-ISO-INDILEUCINE v Indico.

(In. 1) METHYL INDOLE C.H.N s.c.

C,H, CMe CH 195°7 Scatole Skatole (266° 1 V) VD (H-1) 65 2 (calc 65 5)

Occurrence -The chief volatile constituent of human fæces, but not present in that of dogs (Brieger, J pr [2] 17, 129, A 12, 1986) occurs among the products of the putrefaction of albuminous substances (Brieger, Nencki, J pr [2] 17, 98, H 4, 371, E a H Salkowsky, B 12, 651)

Formation —1 By fusing egg albumen with KOH (Nencki) —2 By reducing indigo with tin and HCl, and distilling the product with zincdust A mixture of indole and scatole is thus obtained, and these are combined with picric When the picrates are distilled with conc NaOHAq the indole is destroyed, and the scatole passes over, and may be crystallised from water The yield is 3 pc Scatole prepared in this way has no fæcal odour (Baeyer, B 13, 2339) -3 By heating aniline zinc chloride with gly cerine (Fischer a German, B 16, 710) -4 By adding nitro cuminic acid (6 pts) to amido cuminic acid (obtained by reducing 4 pts of the nitro acid), mixing with baryta (10 pts), drying, and distilling (Fileti, G 13, 358, 378) -5 The phenyl hydrazide of propionic acid is warmed with ZnCl2, and the product distilled with steam (E Fischer, A 236, 138) -6 In small quantity in distilling strychnine with lime (Stochr, B 20, 1108, Lobisch a Malfatti, M 9, 629) -7 By heating its carboxylic acid (Arnold, A 246,

Preparation from pancreas - 2,300 grms pancreas and 500 grms flesh are freed from fat, cut up and put into a loosely covered pot containing 8 litres of water. The whole is left for 5 months at the ordinary temperature the end of the fourth month the odour of skatole The liquid is acidified with acetic distilled. The distillate is acidified appears acid and distilled with HCl and picric acid is added Red needles of skatole picrate, C,H,N C,H2(NO2)3OH, separate This is decomposed by ammonia, and the skatole is distilled over with steam and crystallised from

water (Nencki, J pr [2] 20, 467)

Properties—Glittering plates of powerful fæcal odour, sl sol water—It differs from indole in giving no colour when its solutions are treated with chlorine water Its solution gives with fuming HNO, an opalescence, with KNO, and acetic acid a white pp of the nitrosamine, with CrO, a red amorphous pp in concentrated solutions, and with FeCl, no colour (Brieger, J pr [2] 17, 130) It is not attacked by warm dilute HNO. It colours pine wood moistened with HCl red, this is best seen by dropping pine wood saturated with an alcoholic solution of scatole into cold conc HClAq (Fischer, A 236, 138)

Reactions -1 Potash-fusion yields the corresponding indole carboxylic acid (Ciamician a Magnanini, B 21, 673) -2 By passing CO, over a mixture of sodium and scatole, heated at 240° there is formed indole (In-1)-carboxylic (C a M) -8 With chloroform and NaOEt it yields a chloro methyl-quinoline C, HaClN -4. Bensoic aldshyde and ZnOl₂ form, slowly at 100°, C_cH₃ CH(C_cH_aN), which crystallises from alcohol [142°] (Fischer, B 19, 2989) —5 When adminis-VOL III

tered to animals it appears in the urine in the form of the chromogen of a red pigment and as methyl indyl sulphuric acid C₀H₄N SO₄H (?) (Brieger, H 4, 414, Mester, H 12, 130) Salts -B'₄HCl Ppd in needles when ether

is added to its alcoholic solution (Wenzing, A [168°] Insol ether, v 'sl sol water, 239, 239) v sol alcohol -Picrate B'C,H2(NO2),OH Red needles

Acetyl derivative so called v METHYL-INDYL METHYL KETONE

Dihydride C.H., N & e

C.H. CHMe CH. (232° 1V) at 744 mm Formed by reducing an alcoholic solution of scatole with zinc dust and HCl (Wenzing, A 239, 242) Colourless oil, resembling quinoline and piperidine in odour V sol alcohol, ether, and ligroin Its alcoholic solution stains pine wood, moistened with HClAq, orange It re duces AgNO, and FeCl, on warming It yields a nitrosamine which may be reduced to an oily hydrazine With phenyl thiocarbimide it forms a compound melting at 125° - *B'HCl alcohol and water, insol ether - Oxalate [126°], insol ether -B'2H2PtCl, yellow needles, sl sol water, decomposed by hot water —Pi crate [150°], yellow granular crystals (from benzene)

(In 2) Methyl-indole C.H.N & & C.H. CH SCMe Methyl hetole [60°] (272° 1 V) at 750 mm V.D 4 75 (calc 4 54) (Tread well, B 14, 1466)

Formation -1 By nitrating benzyl methyl ketone with fuming HNO₃, reducing the result ing [21]C₃H₄(NO₂) CH₂ CO CH₃ with zinc dust and ammonia, and distilling with steam (Baeyer a Jackson, B 13, 187, 14, 879) -2 Obtained by heating the phenyl hydrazide of acetone (CH₃)₂C N NHC₆H₅ (1 pt) with ZnCl₂ (5 pts) for half an hour at 100° and then for some minutes at 180° (E Fischer, B 19, 1564, A 236, 124)

Properties - Needles or plates (from ligroin), al. sol hot water, v sol alcohol and ether Smells like indole V sol cold HClAq, but de composed on boiling with conc HClAq colours its solution yellow, and soon gives a yellow amorphous pp which does not give Liebermann's reaction Colours pine wood, moistened with HClAq, red

Reactions —1 kMnO, oxidises it to acetyl o amido benzoic acid —2 Potash fusion yields indole (In 2) carboxylicacid (Ciamician a Magna nini, \hat{B} 21, 673) —3 By heating with sodium in a stream of CO₂ at 240° there is formed methyl ındole carboxylıc acıd (Cıamıcıan a Magnanını, B 21, 671) -4 Reduced by tin and HCl to a hy dride, although sodium amalgam does not act upon it -5 With chloroform and NaOEt it yields chloro methyl quinoline [71°] form and NaOEt yield the corresponding bromo methyl quinoline (Magnanini, G 17, 246) -6 On heating with cone HClAq for 7 hours at 225° there is formed aniline and a liquid base CiaHaN (250°) which smells like quinoline and forms the salts B', H.PtCl, and B'HAuCl, (Magnanini, B 20, 2609) -7 Benzoic aldehyde at 100° forms C.H.CH(C CMe NH), which separates from acetone in colourless shining crystals

ether On boiling with Fe₂Cl₆ in HOAc it is converted into di-methyl rosindole (Fischer, A 242, 378, B 19, 2988) — 8 Nitro-benzoic aldehyde heated with (In 2) methyl indole on the water bath forms the corresponding [3.1] C₆H₄(NO₂) CH(C₉H₈N)₂, small crystals (from acetone), sl sol alcohol, ether, and HOAc This body melts at 263°, and is reduced by zinc dust and ammonia to C_cH₄(NH₂) CH(C_cH₅N)₂ a yellow crystallisable oil (Fischer, A 242, 375) -By fusing with phthalic anhydride and a little ZnCl₂ there is formed an acid C₁₇H₁₈NO₈ pro bably CoH, N CO CoH, CO2H which crystallises from alcohol in colourless prisms, insol water, l sol ether, v sol hot alcohol and HOAc Fischer) -10 On heating with benzoyl chloride nd a little ZnCl2 the products are di methylosındole $C_{23}H_{20}N_2$ and benzoyl methyl ındole 1 On heating with sinc chloride alone, a small uantity of quinoline is formed (Fischer a steche, B 20,819) -12 Diazo benzene chloride ind NaOAc form compact red crystals (from retroleum ether) of C_6H_5 N N $C < C_0H_4 > NH$, 116°], insol water, v sol alcohol, ether, and penzene, m sol petroleum ether This body is plit up again, by reduction, into aniline and $C_0H_4 < NH^{C(NH_2)} > CMe$ mido methyl indole 113°] (Fischer, A 242, 384) -13 When (In 2) nethyl indole (1 pt) is heated with MeI (22 pts) and a little methyl alcohol at 100° for 15 hours,

[247°], msol water, v. sl sol hot alcohol and

here is produced di methyl quinoline dihydride 243°) (Fischer a Steche, B 20, 818, 2199) Salts—B'HI Formed by passing dry HI Salts—B'HI Formed by passing dry HI nto a solution of the methyl indole in ether Wagner, A 242, 388) Flocculent pp, very easily decomposed by water and by moist air B'2H2PtCl, 3aq yellow needles, decomposed by

Acetyl derivative C.H. CH (200°-210° at 40 mm) Formed in small quan ity, together with methyl indyl methyl ketone (qv), by heating (In 2) methyl indole with Ac O and NaOAc The product is extracted with shloroform, and the extract distilled in vacuo (Magnanini, G 18, 95) Pale yellow liquid Decomposed by boiling aqueous KOH into KOAc and methyl indole Yields indole carboxylic acid on fusion with potash KMnO, oxidises it to acetyl o-amido benzoic acid (Ciamician a Mag nanını, B 21, 673)

(B) Acetyl derivative v METHYL INDIL METHYL KETONE

Benzoyl derivative C,H,NBz Formed, together with di methyl rosindole, by heating (In 2) methyl indole with BzCl and a little ZnCl2 on the water bath (Fischer a Wag ner, B 20, 817) Glittering plates (from alcohol), v sl sol hot water, m sol alcohol and ether

Dihydride $C_9H_{11}N$ is $C_6H_4{\stackrel{CH}{\sim}}NH^2>CHMe$ (228° 1 V) at 742 mm **H**ydromethylketole Prepared by reduction of (In 2)-methyl indole with tin and HCl (Jackson, B 14, 883, Wen zing, A 239, 244) Colourless oil with powerful odour Heavier than water Strong base With phenyl-thiocarbimide it forms a compound C14H14N2S, which crystallises from ether in prisins

[101°] —B'₂H₂PtCl₄. orange yellow needles, decomposed by water — Oxalate [130°], crystalline — Picrate [151°], crystalline — Acetyl derivative C.H. (56°) From the dihydride and Ac₂O White needles,

insol water, sol most other solvents

Nitrosamine C.H. NO [55°] Formed by adding NaNO2 to a solution of the hydrochloride of (In 2) methyl indole dihydride (Jackson) Yellow crystals (from ligroin), v sol alcohol, ether, and boiling ligroin On treatment with tin and HCl, methyl indole dihydride is regene rated On reduction with zinc dust and HOAc it yields the hydrazine C_sH₁₀N NH, which crys tallises from ligroin in prisms [41°], and yields a crystalline sulphate and hydrochloride

(In 3)-Methyl indole $C_6H_4 < {
m CH}_{
m NMe} > CH$ (240° 1 V) at 720 mm SG 2 1 0707 Obtained by long heating at about 205° from its carboxylic acid [212°], which is formed by the action of HCl on the phenyl methyl hydrazide of pyruvic acid (Fischer a Hess, B 17, 562) Formed also by heating ω chloro methyl o amido styrene C₆H₄(NHMe) CH CHCl with NaOEt at 135° (Lipp, B 17, 2510)

Properties — Yellowish liquid, nearly insol

water, v sol alcohol, ether, and benzene Vola tile with steam A chip of pine wood, dipped in HClAq, is coloured violet red by its vapour or solution It dissolves in cone HClAq and is reppd by addition of water Fuming nitric acid added to (In 3) methyl indole suspended in water gives a deep red colour and finally a red pp

Reactions -1 Analkaline solution of bromine

(NaOBr) converts it into di bromo methyl oxin dole C₈H₂Br₂NO, which crystallises in transpa rent tables, melting at 204° It is converted by heating with alcoholic potash into methyl \$\psi\$ isatin, which is ppd, after boiling off the alcohol, by adding HCl = 2 (In 3) methyl indole (2 mols) heated with benzoic aldehyde (1 mol) and ZnCl₂ for 2 hours on the water bath forms C_eH_s $CH(C \leqslant \stackrel{C_eH}{CH} > NMe)_2$, which crystallises in colourless prisms [197°], insol water, sl sol al cohol and ether, v sol hot acetone and HOAc It yields a red dye on heating with FeCl in HOAc (Fischer, A 242, 377, B 19 2988) — 3 On fusing equal weights of phthalic anhydride and (In 3) methyl indole with a little ZnCl, at 100° there is formed C₈H₄ C₂O₂(C₉H₈N), which crystallises from acetone in colourless prisms [300°] It is insol water and alkalis, v sl sol ether and alcohol, but v sol hot acctone (Fischer, A 242, 382, B 19, 2989) —4 Scarcely attacked by MeI at 100°, but at 120° it appears to yield a methyl quinoline dihydride (Fischer a Steche, B 20, 2199)

Picrate CoHoNCoH2(NO2)sOH [150°] Long dark red prisms or needles, v sol benzene, sl sol ether Decomposed by alcohol

Chloro derivative v Di-chloro METHYL-

Dihydride $C_0H_4 < \frac{CH_2}{NMe} > CH_2$ (216° 1 V) at Formed by reducing (In 3) methyl indole with zinc dust and cone HClAq (Wenzing, A 239, 246) Liquid, sl sol water, v sol alcohol and ether, volatile with steam Most of itc

salts dissolve in alcohol and water -B'sHsPtCls:

yellow needles, decomposed by boiling water — Oxalate [105°] —Picrate [155°], yellow tables (from benzene)

CMe CH C CH (B 2) Methyl-indole CH CH CNH

Tolindole [585°] Formed by heating at 240° its carboxylic acid, which is obtained from the p tolyl hydrazide of pyruvic ether (Raschen, A 239, 226) Needles (from water), m sol hot water, v sol alcohol, ether, benzene, and ligroin Volatile with steam Reacts like indole with pine wood and with introus acid—Picrate B'C₄H₂(NO₂)₃OH [151°] Red needles (from water)

(In 1,2) Di methyl indole C, H, N 2.6

C₆H₄< CMe SCMe. [108°] (285° 1 ♥) Formed by heating the phenyl hydrazide of methyl ethyl ketone with ZnCl, at 180° (E Fischer, B 19,1565, A 236, 126) Formed also by heating bromo acctyl propionic acid CH, CO CHBr CH, CO2H (1 pt) with aniline (3 pts) at 100° (Wolff, B 20, 427, 21, 123) Obtained likewise by heating at 225° (Fischer)

C₆H.<

Properties —White plates (from dilute alco hol) Smells like indole V sl sol hot water, v e sol alcohol and ether, sl sol cold ligroin Dissolves in conc HClAq but is reppd on dilution with water Does not colour pine wood Reactions —1 NaNO, added to its solution

in HOAc forms a nitrosamine [63°], crystallising in yellow needles, v sl sol water, v sol alcohol By zinc dust and HCl it is re converted into di methyl indole It exhibits Liebermann s reaction -2 MeI in MeOH converts it into tri methyl quinoline dihydride

Picrate B'C₆H₂(NO₂)₈OH [157°] Brown needles (from alcohol)

Dihydride C_eH₄< CHMe CHMe (231°) at

Formed by reducing di methyl indole with zinc dust and HClAq (Steche, A 242, 371) (In 2,3) D1 methyl indole C10H11N te

 $C_{\rm e}H_{\rm 4}<_{
m NMe}^{
m CH}>$ CMe [56°] Formed by heating the phenyl methyl hydrazide of acetone (1 pt) with zinc chloride (5 pts) for 3 hours at 130° (Fischer, B 19, 1565, Degen, A 236, 153) Formed also by heating its carboxylic acid C₆H₄ C(CO₂H) CMe at 200° (D) needles, v sol alcohol, ether, benzene, and ligroin, v sl sol water, v sol conc HClAq May be distilled without decomposition It gives the pine wood test very distinctly Nitrous acid The picrate forms a complicated product The hydride crystallises in dark red needles 18 v sol weak acids

(In 1,3) D1 methyl indole $C_{e}H_{4} < \frac{CMe}{NMe} > CH$ (230°-255°) Formed by heating the phenylmethyl hydrazide of n propionic aldehyde (1 pt) with ZnCl₂ (5 pts) at 135° (Degen, A 236, 163) Oil

(B 2-In-3) Di-methyl-indole C, H, N i.e CMe CH C CH Methyl - p - tolindole CH CHÜNMe

(242°-245°) Formed by heating acid at 225° (Hegel, A 232, 216) Formed by heating its carboxylic Liquid, volatile with steam, v sol. alcohol, ether, and benzene Dyes pine wood, moistened with HCl, red. Fuming HNO, gives a red colour and, finally, a The picrate is crystalline

CMe CH C CH (B 2, În 2)-Di methyl indole CieHiiN 1.4.

Methyl - p tolindole CH CH C NH [114°-117°] Formed by heating the p-tolylhydrazide of acetone with ZnCl2 (Raschen, A May be distilled without decompo-Almost insol hot water, v sol hot alco sition hol, ether, and benzene -B'C,H2(NO2)2(OH) [155°] Dark red needles (from benzene)

(B 4, In 2) Di methyl indole C_{1e}H₁₁N CH CH CH CH Methyl o-tolundole

tained by the action of heat on its carboxylic acid, which is derived from the o tolyl methylhydrazide of pyruvic acid (Hegel, A 232, 220) Liquid, smelling like indole, volatile with steam Dyes pine wood, acidified by HCl, violet red. Behaves like indole towards nitrous acid

Di-methyl indole C₁₀H₁₁N (275) Formed by allowing a solution of the hydrochloride of (a) di methyl dipyrrole in dilute H.SO, to stand for some time in the cold (Dennstedt, B 21, 3439) Liquid, volatile with steam—Picrate B'C₆H₂(NO₂)₃OH [156°] Dark red silky needles

(from benzene)

Di methyl indole C₁₀H₁₁N (c 270°) Formed from (3) di methyl dipyrrole in the same way as the preceding isomeride (D) Liquid Smells like scatole —Picrate B'C.H (NO.),OH [149°] Red silky needles

(In 1,2,3) Tru methyl indole C, H, N C_eH₄<CMe CMe (280°) Formed by heating di methyl indyl acetic acid for several hours at 210° (Degen, A 236, 160) Formed also by heating the phenyl methyl hydrazide of methyl ethyl ketone with ZnCl₂ at 180° (D) Yellow oil with characteristic odour Miscible with alcohol and ether Gives no colour to pine wood Picrate B'C,H2(NO2),OH [150°] Dark red needles (from hot benzene)

CH CH C CMe CMe (B 4, In 1, 2) Tri methyl indole C, H, N t.e

[79°] (283° uncor) CH CMe C NH Formed by heating bromo acetyl propionic (bromo levulic) acid CH, CO CHBr CH₂ CO₂H with o toluidine (Wolff, B 21, 3362) White plates, v sol alcohol, chloroform, and petroleum ether, v sl sol water Volatile with steam — Picrate B'C₄H₂(NO₂)₃OH [152°] Purple red

(B 2, In 1,2) Tri-methyl indole C,1H,2N : 6. CMe CH C CMe CMe [1219] (297° cor)

CH CH CNH / Formed by warming & bromo acetyl propionic acid (1 pt) with p toluidine (3 pts), and finally heating the mixture to boiling (Wolff, B 21, 3361) Plates, v sol alcohol, chloroform, and petroleum ether, v sl sol water Does not give the pine wood reaction The solution in HOAc, mixed with FeCl, becomes green on boiling, and

finally blue Picrate B'C_eH₂(NO₂)₃OH [189°] Brownish-red needles, v sol benzene and alsohol

Netrosamene $C_{,H_{\circ}} < \frac{CMe}{N(NO)} > CMe$ [73°] Golden-yellow needles, v e sol alcohol and HOAc, al sol water

Tetra-methyl-indole C₁₂H₁₅N (285°) Lightyellow oil, with characteristic odour (Dennstedt, B 22, 1924) Picrate B'C₂H₂(NO₂)₃OH [100°] Shining red needles

METHYL-INDOLE ACETIC ACID v METHYL INDYL-ACETIC ACID

 $\begin{array}{cccc} (In & 1)\text{-}\mathbf{METHYL}\text{-}\mathbf{INDOLE} & (In & 2)\text{-}\mathbf{CARB}\text{-}\\ \mathbf{OXYLIC} & \mathbf{ACID} & \mathbf{C_{10}H_2NO_2} \ \imath \ e \end{array}$

C.H. CMe C CO.H Scatole (B)-carboxyluc acid [165°] Formed by saponifying with alcoholic potash its ether which is obtained by boiling with alcoholic hydrogen sulphate (10 pc), the phenyl hydrazide of ethyl glyoxylic ether CH. CH. C(N.2HPh) CO.H (Wishicenus a Arnold, B 20, 3395, A 246, 335) Formed also by heat ing scatole with sodium in a current of CO.2 at 240° (Chamician a Magnanini, G 18, 61, B 21, 672, 1927, Rend Accad Linc [4] 4, 740) Thin white needles (from boiling water), v sol alcoholic solution is coloured deep red by FeCl. On heating above 165° it is split up into CO.2 and scatole [95°]—AgA' white powder, insol water

Ethyl ether EtA' [134°] Needles (from alcohol), insol water, v e sol benzene and ether

(In 1)-Methyl-indole carboxylic acid
C_{1c}H₂NO₂. Scatole (a) carboxylic acid [164°]
(Possibly identical with the preceding acid)
Occurs among the products of the putrefaction
of serum albumen, and of muscular tissue (H a
E Salkowsky, B 13, 191, 2217, H 8, 23, 9,
8) Small plates (from benzene) Decomposed
on heating above its melting point into CO₂ and
scatole V si sol cold water, v sol alcohol and
ether, m sol benzene FeCl, colours its dilute
solution (containing HCl) violet on boiling
Nitrous acid colours its dilute solution cherry
red, and presently gives a pp Bleaching powder
colours a dilute solution, acidified by HCl, purple,
this reaction, and that with introus acid, are not
exhibited by (In 1)-indole (In 2) carboxylic acid
—AgA' Sparingly soluble pp

(In 2) Methyl-indole (In 1)-carboxylic acid
C CO₂H

Methyl ketole carboxylic
NH CMe

acid [172°] or [183°] Prepared by heating (In 2)-methyl indole (10 g) mixed with sodium (36 g) in a current of dry CO, first at 235° and finally at 315°, the unaltered methyl-indole is removed by steam distillation, and the acid re crystallised from acetone (Ciamician a Magnanin, G 18, 60, B 21, 672, Rend Accad Linc [4] 4, 740) White crystalline rowder, completely decomposed at its melting point into CO, and methyl indole (methyl ketole), this decomposition is partially effected by merely boiling the aqueous solution. Sl. sol water and benzene, v sol alcohol and acetone. It gives white pps with lead and mercuric salts, and a

green pp with a cupric salt —AgA' white crys talline pp

(In 3)-Methyl-indole (In 1) carboxylic acid C₂H₄ C(CO₂H) CH [212°] Obtained by heating the phenyl methyl hydrazide of pyruvic acid (1 pt) with 10 pc aqueous HCl (15 pts) on the water bath (E Fischer a Hess, B 17, 559) White needles, v sol hot alcohol, ether, and benzene, sl sol hot water, nearly insol cold water Its solution in H₂SO₄ is red By prolonged heating at its melting point it is split up into CO₂ and (In 3)-methyl-indole Readily oxidised by KMnO₄ An alkaline solution of Br or Cl oxidises it to methyl-ψ isatin and CO₂ (B 4)-Methyl-indole (In 2) carboxylic acid

(B 4)-Methyl-Indole (1n 2) value (1n 2) CH CH C OH CH CH CO OH [171°] Formed by CH CMe C NH saponfying with alcoholic potash its ethyl ether which is obtained by heating the o-tolyl hydra

zide of pyruvic ether (1 pt) with ZnCl₂ (1 pt) at 220° (Raschen, A 239, 228) Needles (from water), v sol alcohol, ether, and HOAc (B 2)-Methyl-indole (In 2) carboxylic acid

CMe CH C CH

CH CH CNH

CH CH CNH

its ethyl ether which is obtained by heating the p-tolyl hydrazide of pyruvic ether with ZnCl, at 220° (Raschen, A 289, 228) Needles (from water), m sol hot water, v sol alcohol, ether, ohloroform, and HOAc Decomposed on fusion

into CO₂ and (B 2) methyl indole

Ethyl ether EtA' [160°] Colourless

needles or plates (In 2, 3) D1 methyl-indole (In 1)-carboxylic acid $C_{11}H_{11}NO_2$ i.e. $C_0H_1 < \begin{array}{c} C(CO\ H) \\ NMe \end{array} > CMe$

[185°] Formed by saponifying its ether which is obtained by heating the phenyl methyl hydra zide of acetoacetic ether with ZnCl₂ (Fischer, B 19, 1569, Degen, A 236, 157) Six-sided plates, m sol hot alcohol and chloroform, sl sol water, ether, benzene, and ligroin Splits up at 200° into CO₂ and (In 2 3) di methyl indole The Na salt is insol cone NaOHAq The Ag salt is insol NH₂Aq Colours pine wood

salt is insol NH,Aq Colours pine wood

Ethyl ether Eth' [95°] Colouriess
needles (from alcohol-ligroin), v sol alcohol
ether, benzene, and chloroform, sl sol ligroin

(B 4, In 3) Di-methyl indole (In 2)-carbexplic acid C₁₁H₁₁NO₂ ie CH CH CCH

CH CH CCH CO₂H [210°] Formed by CH CMe C NMe warming the o-tolyl methyl-hydrazide of pyruvic acid (1 pt) with phosphoric acid (20 pts of S G 1 17) on the water bath (Hegel, A 282, 220) Colourless needles (from benzene), v e sol alcohol Splits up on heating into CO₂ and the corresponding di methyl indole When its alka line solution is warmed with NaOCl and the product heated with water there is formed dimethyl \(\psi \) isatin C₂H₂Me \(\begin{center} \mathbb{CO} \text{NMe} \rightarrow \mathbb{CO} [157°] \end{center} \]

nde of pyruvic acid (1 pt) with HCl (20 pts of 10 pc), the acid being ppd (Hegel, A 232, 216) Needles (from hot alcohol), al sol ether, sol hot penzene, chloroform, and glacial HOAc, insoligroin Forms the corresponding dimethylndole on heating A neutral solution of its Na salt gives with NaOCl a yellow crystalline pp 135°], which on boiling with water is changed io di methyl ψ isatin C_eH₃Me<CO crys allising in red needles [148°]

METHYL INDOXAPHTHENE C, H, С,Н, СМе СН Methyl - undene (206°)(Roser), (201°) (Von Pechmann, B 16, 516) Formed by distilling methyl indonaphthene carpoxylic acid with soda lime (Roser, A 247, 159) Transparent highly refractive liquid, smelling somewhat like naphthalene Absorbs oxygen from the air, becoming gummy On heating with conc HClAq it also becomes gummy, and H SO, has a like effect By heating with HIAq at 180° it is converted into a solid body, fusible under water, v sol ether, sl sol alcohol

Picric acid compound

C₁₀H₁₀C₈H₂(NO₄)₈OH [76°] U powder (Von Miller, B 23, 1882) Unstable orange

CARBOXY METHYL INDONAPHTHENE LIC ACID C11H10O2 te C6H4CCH2CO2H 'Dihydronaphthoic' acid [200°] Formed by gently warming benzyl aceto acetic ether (1 pt) with conc H.SO, (7 pts), and pouring the product into water (Von Pechmann, B 16, 516, Roser, B 20, 1574, A 247, 158) White needles (from alcohol), almost insol water, m sol hot alconol and ether Crystallises from glacial acetic acid in prisms (containing HOAc) May be distilled with slight decomposition, but when boiled for a long time it splits up into CO2 and methyl indonaphthene On oxidation it yields phthalic acid

Methylether *MeA' [78°] Small needles, v sol alcohol and ether

C_eH₄<CH₂CBr CO₂H Dı - bromide [215°] Formed by exposing the acid to brominevapour White crusts (from ether) On warm ing with HOAc it gives off HBr and leaves $C_eH_4 < \stackrel{CMeBr}{CH} > C CO_2H$ [245°], which forms a methyl ether melting at 100°

Methyl ether C10H2Br2CO2Me. [157°] White needles, sl sol methyl alcohol

METHYL INDONAPHTHENE DIHYDRIDE CARBOXYLIC ACID C11H12O2 te

C.H. CHMe CH CO.H Methyl-hydrindonaphthene carboxylic acid [80°] (300°-310°) Formed by the action of sodium amalgam on an alkaline solution of methyl indonaphthene carboxylic acid (Roser, B 20, 1574, A 247, 165) Small needles (from hot water), v sol alcohol and ether, scarcely volatile with steam On continued heating above 310° it becomes viscid, but the crystalline acid is reproduced on treating this viscid mass with alkalis -AgA' -BaA', 2aq needles (from alcohol), v sol water METHYL INDONAPHTHOQUINONE

C1.H.O2 2.6. C.H. CO CHMe. Methyl-da-keto-

hydrindene [85°] (c 150° at 18 mm) Formed by the action of sodium on a mixture of ethyl propionate and phthalate (Wislicenus a Kötzle, A 252, 80) Blunt pyramids (from alcohol) or needles (from light petroleum), sol ether and hot water The sodium derivative C16H,NaO3 crystallises in small dark-red prisms

Di-oxim C_eH₄ C(NOH) CHMe [1177]. Needles, sol alcohol, ether, alkalıs, and HOAc Mono-phenyl-hydrazide

 $C_0H_4 < CO \xrightarrow{C(N_2HPh)} CHMe$ [164°] Crystals, \forall . sol ether and benzene Forms a green solution in HOAc

Di-methyl-indonaphthoquinone C, H, O. t.s C_eH_•COCMe [108°] (c 250°) Formed by heating methyl indonaphthoquinone with MeI and MeOH at 100° (W a K) V sol alcohol, ether, and benzene

Phenyl hydrazide

C₀H₄ C(N,HPh) CMe₂ [184°-187°] Slender yellowish prisms (from alcohol), sol ether and HOAc FeCl, colours its solution in H2SO, intensely dark green

METHYL INDOPHENINE v Indophenine METHYL-INDYL ACETIC ACID C,H,1NO. CH2.CO2H

Te C'H' CNE [195°-200°]

Formed by warming the phenyl hydrazide of acetyl propionic (levulic) acid with ZnCl₂ at 125° (E Fischer, B 19, 1565, A 236, 149) Colourless plates, sl sol hot water and chloroform, m sol ether, v sol hot alcohol, v e sol acetone and hot HOAc Nitrous acid yields a nitrosamine At 225° it is split up, slowly into CO₂ and di methyl indole. Its picric acid compound crystallises in slender dark red needles

Di-methyl-indyl-acetic acid CigHisNO, s.c. CH, CO,H

O.H. NMe CMe [188°] Formed by saponification (by alcoholic KOH) of its ether. which is obtained by warming the phenyl methylhydrazide of acetyl propionic ether with ZnCl, (Fischer, B 19, 1568, Degen, A 286, 158) Colourless plates, sl sol water, ether, and benzene, v sol alcohol and chloroform Its alkaline salts are v e sol water, but ppd on addition of caustic alkalis At 210° it is split up into CO, and (In-1,2,3) tri methyl-indole Does not give the pine-wood reaction

METHYL INDYL KETONE v (β) Acetyl-

INDOLE (In 1) METHYL INDYL METHYL KETONE C,H,NO ce. C,H, CMe CO CH, Acetyl-[148°] Formed by heating (In-1)methyl indole (scatole) (1 g) with AcCl (10 g) and ZnCl_2 ($\frac{1}{2}$ g) (Magnanini, G 18, 99, B 21, 1938) Long needles (from dilute alcohol), insol. cold water, v sol hot alcohol and acetone, m sol ether Volatile with steam Not affected by KOHAq, but conc HCl forms scatole cone H₂SO₄ gives a purple solution Picrate [156°] Yellow needles, at sol.

cold, v sol hot, benzene

Oxem C.H. CMe C C(NOH) CH. [119°]. Small needles, decomposed by acids and alkalis, reproducing the ketone

(In. 2)-Methyl-indyl methyl ketone

CO CH,
Acetyl methyl ketole
CMe
CMe

[196°]. Formed by heating (In 2) methyl indole (methyl ketole) (1 pt) with Ac₂O (5 pts) and NaOAc (1 pt) for six hours with inverted condenser (Jackson, B 14, 879, Fischer, A 242, 879) Colourless needles (from acetone), sl sol water, v sol alcohol and hot benzene Dissolves in HClAq Not decomposed by boiling NaOHAq, but boiling cone HClAq regenerates the ketone KMnO₄ oxidises it to acetyl amido benzoic acid (Magnanim, G 18, 97)

Phenyl hydraside C₁,H₁₇N₂ 16 C(N₂HPh) CH₂

C.H. CMe [c 136°] Formed

by heating the ketone with phenyl hydrazine hydrochloride and NaOAc Colourless plates, m sol hot benzene, v sl sol petroleum ether

DI-METHYL INOSITE v DAMBONITE METHYL-IODAMINE v METHYLAMINE

METHYL IODIDE CH,I Iodo methane Molw 142 (428°) (Dobrner, A 243, 23), (423°) (Perkin, C J 45, 459) S G § 2 3346 (D), 152 2252, 252 2529 (P) S 008 at 15° (Bardy a Bordet, A Ch [5] 16, 569) C E (0°-10°) 00118 (D) S V 641 (Lossen, A 254, 69), 648 (Ramsay), M M 9 009 at 195° H F p (gas) +3420 H F v (gas) 2840 (Thomsen, Th) Obtained by distilling phosphorus (1 pt) with iodine (8 pts), dissolved in moist methyl alcohol (14 pts), or phosphorus (60 g) with iodine (1000 g) and methyl alcohol (500 g) (Dumas a Péligot, A 15, 30, Pierre, A 56, 147, Landolt, A 84, 44, Hofmann, C J 18, 69) Prepared also from red phosphorus (10 pts), MeOH (35 pts), and I (100 pts) (Personne, J 1861, 607, Butlerow, B 6, 561), and from KI, MeOH, and gaseous HCl (De Vrij, J 1857, 441) The distillate is washed with water and rectified over CaCl₂ and lead oxide Colourless, slightly combustible liquid Not at acked by gaseous HCl

Reactions—1 Chlorine converts it into MeCl—2 When heated with zinc it forms IZnMe—The moist copper zinc couple forms methane (Gladsone a Tribe, C J 26, 682)—8 When heated with alloys of K or Na with As or Sb it yields methides of arsenic or an timony—4 With Mg and Al it forms methides—5 When heated in a sealed tube with aqueous NH, it forms mono, di, and tri methylamine and NMe,I—6 With EtOH at 125° it forms EtI and MeOEt (Busse a Kraut, A 177, 272)—7 Heated with water (15 pts) at 100° it is converted into methyl alcohol (Niederist, A 196, 350)—8 With H₂S and water it forms MeI(H₂S)₂28aq (Forcrand, A Ch [5] 28, 21)—9 Sulphur at 160° to 190° forms SMe₂I and other products (Klinger, B 10, 1880)

other products (Kinger, B 10, 1880)

Hydrate (MeI)₂ aq [-4°] (F), [4 8°]
(Villard, C R 111, 185) Formed by passing a current of most air through the iodide (Forcrand, C. R 90, 1491)

METHYL-IODOFORM v TRI 10DO ETHANE

METHYL-ISATIC ACID v ISATIC ACID METHYL-ISATIN v ISATIC METHYL-ISATOIC ACID v ISATOIC ACID METHYL-ISATOID v ISATOID

METHYL-ITACONIC ACID C.H.O. [166]. A product of the distillation of methyl paraconic acid (Fränkel, A 255, 37) Formed also by heating a solution of methyl citraconic acid at 150° in sealed tubes Prisms, sol water, insolubility of the sealed tubes Prisms, sol water, insolubility

Ag,A"
TETRA METHYLIUM HYDROXIDE v
Methylo hydroxids of Trimethylamine

DĬ METHYL-KETINE 18 TETRA METHYL PYRAZINE

DI-METHYL-KETOL v METHYL OXYETHYL KETONE

METHYL-KETOLE v (In 2) METHYL INDOLE

DI METHYL-KETONE 18 ACETONE

D1 methyl di ketone $C_4H_4O_2$ i e CH_2 CO CO CH_4 D1 acetyl (88°) SG 27 9734 S 25 at 15° Formed by heating it dicarboxylic acid (ketipic acid) either by itself or with dilute H_2SO_4 (Fittig, B 20, 3179, A 249, 200) Formed also from its mono oxim (nitroso methyl ethyl ketone) by successive treatment with $NaHSO_3$ and dilute acid CH_3 CO CMe $NOH + H_2SO_3 + H$ O

= CH, CO COMe + NH, SO, H (Von Pechmann, B 20, 3162) Most easily prepared by saponi fying methyl aceto acetic ether with dilute (3 pc) alkalı, treating the product with NaNO, and $\rm H_2SO_4$, removing alcohol by distillation, adding dilute $\rm H_2SO_4$ (20 vols of 15 pc), and distilling with steam (Von Pechmann, B 21, 1411) Yellow mobile liquid, smelling like acetone and quinone, miscible with alcohol and ether composed by alkalis or hot alkaline carbonates Forms metallic derivatives of trimethyl glyoxal ine with ammoniacal solutions of silver nitrate and of cuprous chloride With alcohol it forms an unstable compound C.H.O.2HOEt, boiling at 75° With water it forms a crystalline hy drate (C,H,O.), 2aq, insol water, alcohol, and Yields a very unstable compound with Combines with NaHSO₃ eth**er**

SO₂ Combines with Names So₃

Reactions —1 With HCy it forms the nitrile of di oxy di methyl succinic acid —2 Bromine dissolved in CS₂ forms a di bromo derivative C₄H₄Br₂O₂ [117°] —3 Ammonia forms tri

methyl glyoxalıne CHMe N CMe [133°] (271°).

4 When warmed with o tolylene diamine acet ate it is converted into tri methyl quinoxaline O_oH_4 Me< N CMe>, which crystallises from light petroleum in prisms [91°] (270°) —5 Aniline forms the anilide PhN CMe CMe NPh, which crystallises from alcohol in lustrous sulphuryellow scales [183°], v sol ether, m sol alcohol, insol water —6 On adding dilute aqueous NaOH or Na₂CO₂ to an aqueous solution of the diketone until it becomes colourless, then at once acidifying with dilute H_2 SO₄ and extract-

ing with ether, the product is di methyl quinogen CH, CO CMe CH CO CO CH, a yellowish bitter syrup, which forms a phenyl-hydrazide $C_8H_{10}(N_2HPh)$, [205°], and is converted by excess of alkali into p xyloquinone -7 Heated with an aqueous solution of urea it forms di methyl glycolurite C₂H₁₀N₁O₂ (Franchi uont a Klobbie, R T C 7, 251) —8 Reduced in alkaline solu-tion to a product (CH₂ CO CH(OH) CH₂?), which instantly reduces Fehling's solution in the cold

Mono-oxim CH, CO C(NOH) CH, Iso nitroso methyl ethy' ketone (186°)[74°] Formed by treating VD 351 (calc 349) methyl aceto acetic ether (1 mol) with aqueous KOH (3 mols), followed by nitrous acid (V Meyer a Zublin, B 11, 322) Prisms (from chloroform) or plates (from water), v e sol alcohol, ether, and chloroform Decomposed by heating with dilute HClAq at 140° into ammonia and acetic acid Boiling cone HClAq yields HOAc, hydroxylamine, and a little of the dioxim (Schramm, B 16, 177) By boiling with dilute H₂SO₄ it is split up into hydroxylamine and the diketone (Von Pechmann, B 20, 3213) Treatment with aqueous NaHSO, and dilute H₂SO₄ also forms di methyl diketone (Von Pech mann, B 20, 3162) Alkaline K.FeCy, oxidises it, even in the cold, to acetic and nitrous acids (Gutknecht, B 12, 2290) On reduction by SnCl, and HCl, followed by removal of tin by H,S and addition of alkali, tetra methyl pyrazine is obtained But if the solution is allowed to stand when acid another base is got (Braun, B 22, 559)

Methyl ether of the mono oxim CH, CO C(NOMe) CH, (125° uncor) Colour less oil, lighter than water (Ceresole, B 16,

Di oxim CH, C(NOH) C(NOH) CH, thyl ethyl acetoximic acid [234°] by the action of hydroxylamine on the mono oxim (Schramm, B 16, 179, Auwers a V Meyer, B 21, 3527) or on the diketone (Fittig, A 249, 204) Small colourless needles, insol water, v sol alcohol and ether May be sublimed

Oxim phenyl hydraside CH₃ C(NOH) C(N₂HPh) CH₂ [158°] Formed from the oxim and phenyl hydrazine (Von Pech mann a Wehsarg, B 21, 2997) Large crystals (from alcohol) Its solution in H₂SO₄ is coloured bluish violet by FeCl₂

Phenyl-hydrazide

CH, CO C(N2HPh) CH, [133°] Formed by running a solution of diazobenzene chloride into one of methyl acetoacetic acid, the reaction being completed by adding a solution of NaOAc (Japp a Klingemann, B 21, 549, A 247, 218, Von Pechmann, B 21, 1411) Yellow tables Forms a yellow solution in (from benzene) cone H2SO4

Di-phenyl di hydraside CH, C(N, HPh) C(N, HPh) CH, [243°] (Japp), [239°] (Fittig) Formed by treating the mono phenyl hydrazide with phenyl hydrazine (Japp, A 247, 218), or by the action of phenyl-hydrazine on an ethereal solution of di methyl di ketone (Fittig, A 249, 203, Von Pechmann, B 20, 3164) Formed also by heating the phenyl hydrazide of pyruvic acid (Japp a. Klingemann, B 21, 550) Yellowish needles, almost insol water, alcohol, and ether, al sol

enloroform, m sol acetone and hot benzene Dissolves in cold cone H₂SO₄ forming a brown solution, which after some time becomes dirty wine red, appearing green in thin layers K2Cr2O, in HOAc oxidises it to the 'osotetrazone CH, C N NPh

 CH_1 , which crystallises in matted red

needles [169°], insol water, sol chloroform and benzene, m sol ether, sl sol acetone and alco hol, almost insol HOAc This 'osotetrazone' is reduced to the original diphenyl dihydrazide by warming with phenyl hydrazine HCl con verts the 'osotetrazone' into an 'osotriazone' CH, CN,

NPh, which is a very weak base, CH, CN [35°], (c 255°), insol water, sol alcohol and

ether (Von Pechmann, B 21, 2759)

DI METHYL DI-KETONE DICARBOXYLIC ACID C.H.O. 10 CO.H CH. CO CO CH. CO.H Dr. keto adopte acid Ketipac acid Ketipatic Ketipatic acid Oxalyl di acetic acid Obtained by warm ing its ethyl ether with cold conc HClAq (Fittig a Daimler, B 20, 203, A 249, 183) White amorphous powder, insol or v sl sol cold water, alcohol, chloroform, CS2, benzene, and petroleum ether On heating alone or with dilute H.SO, it

is converted into dimethyl diketone
Ethyl ether Et₂A" [77°] Prepared by warming oxalic ether with chloro-acetic ether and amalgamated granulated zinc at 80° for three days The mass is extracted with water and the insoluble portion treated with dilute H₂SO₄, and the solution so obtained extracted with ether The ether is distilled off, and the ketipic ether left recrystallised from alcohol (Fittig a Daimler) Formed also by the action of NaOEt and oxalic ether on acetic ether (Wis licenus, B 20, 589, A 246, 328) Colourless plates or prisms, insol cold water, v sol ether and chloroform, m sol hot alcohol, benzene, and CS₂ Decomposed by boiling water FeCl, colours its alcoholic solution deep red

Reactions—1 Bromine added to a warm solution of the ether in CS₂ forms CO₂Et CBr₂CO CO CBr₂CO₂Et [119°], which is converted by ammonia into oxamide and di bromo acetamide [156°] Bromine added to a solution of ketipic ether in cooled CS₂ forms CO₂Et CHBr CO CO CHBr CO₂H, which is de posited in colourless plates [70°] -2 Chlorine passed into a boiling solution of the ether in chloroform forms CO2Et CCl2 CO CO CCl2 CO2Et [93°], which is also produced by chlorinating dı oxy quinone dicarboxylic ether (Böniger, B 22, 1285) -3 Phenyl hydrasine forms a phenyl hydrazide

CO₂Et CH₂ C(N₂HPh) C(N₂HPh) CH₂ CO₂Et crystallising from chloroform in light yellow needles [160°-180°]

DI-METHYL-KETOXIM v ACETOXIM

METHYL-LEPIDONE v OXY DIMETHYL-QUINOLINE

METHYL-PARA-LEUCANILINES v METHYL-TRI AMIDO TRI PHENYL-METHANES

METHYL LUTIDONE v OXY TRI METHYL-PYRIDINE

METHYL-PSEUDO-LUTIDO-STYRIL v Oxy TRI METHYL PYRIDINE

DI-METHYL-MALEIC ACID C.H.O. ve.
CO.H.OMe OMe CO.H. Pyrocinchonic acid
Di-methyl-fumeric acid. Di-methyl-ethylene
di-carboxylic acid Butylene dicarboxylic acid

Formation —1 Its anhydride is formed by the dry distillation of cinchonic acid C,H,O, (Weidel a. Schmidt, B 12, 1151; Weidel a Brix, M 3, 608) —2 The anhydride is formed by distilling the mother liquor from the preparation of terebic acid by oxidation of turpentine with HNO, (Roser, B 15, 1318) —3 By heating the lactone CH, C(CO,H) CH(CO,H) CH, CO at 180°

(Rach, A 234, 39) —4 Together with di-chloro di-methyl succinic acid

CO₂H CClMe CClMe CO₂H by the action of reduced silver upon $d_{1-\alpha}$ chloro propionic acid (Otto a Beckurts, B 18, 825) —5 By the action of reduced silver upon di chloro di methyl succinic acid (O a B) —6 The anhydride is formed by treating either 'anti' or 'para' dimethyl-succinic acid in the fused state with bromine (Bischoff a Voit, B 23, 646)

Properties — The free acid is unstable, on adding an acid to its salts the anhydride is at once ppd The sodium salt gives a dark red colouration with FeCl₂, and crystalline pps with

Pb(NO₈)₂ and HgCl₂

Salts —Na₂A"₂aq white crystalline solid —Na₂A"1½aq —CaA" small needles, less sol hot water than cold (Roser) —CaA"aq small white plates (O a B) —BaA" white glustening plates, more sol cold water than hot —Ag₂A' sparingly soluble pp, decomposed on heating into Ag₂O and the anhydride

Methyl ther Me₂A" Colourless oil Ethyl ther Et₄A" (240°) Oil Formed by treating the anhydride with alcohol and HCl CMe CO.

Anhydride | [96°] (223°)

VD 42 (calc 43) Formed as above Crystal lises in glistening white leaflets or trimetric tables (from water), abc = 626 1 1 521 or 201 3321 V sol alcohol, ether, and benzene, al sol cold water The aqueous solution is acid and has a sweet but burning taste Volatile with steam Readily sublimes Not attacked Chromic acid mixture oxidises it to by HNO, acetic acid and CO2. Reduced by sodiumamalgam to s-di-methyl-succinic acid [194°] and two isomeric acids [241°] and [120°], the last acid being methyl-ethyl-malonic acid (Otto a Rössing, B 20, 2736) Cone HIAg at 220°, and Conc HIAq at 220°, and zinc filings in water or ammonia also reduce it to s di methyl succinic acid The anhydride is not attacked by PCl, or AcCl It is dissolved by aqueous alkalis, forming the sodium salt of the acid Potash fusion yields oxalic acid By heating with bromine and water at 100° there is formed di bromo-acetic acid When it is dissolved in benzene and shaken with phenyl-hydrazine in the cold the anhydride forms the compound CH, O(CO N,H,Ph) CMe CO O N,H,Ph, which, when shaken with HClAq, regenerates the anhydride, but when heated at 115° yields CO, CMe CO NH

phenyl-hydrazine, and | | [129°], which CMe CO NPh

erystallises from dilute alcohol in yellow mono- and benzene Fumi clinic prisms, and yields di methyl maleic acid forming CO₂ and N₂O

wnen warmed with KOHAq or HCiAq (Otto a. Holst, J pr [2] 42, 67)

CMe COCl

Chlorade | (220°-230°) Formed OMe COCl

by the action of PCl, on the anhydride (O a H) Yellow oil When acted upon by the Na salt it yields the anhydride NH, converts it into the imide Phenyl-hydrazine forms the compound CMe CO.

N NHPh [187°] isomeric with the

body melting at 129° (v supra)

Imide | NH [118°] Formed by CMe CO

heating the anhydride with alcoholic NH, Triclinic plates, m sol hot water, v sol alcohol May be sublimed — *B'₂H₂PtCl₄

Anrilade | NPh [96°] Formed

by heating the anhydride with aniline at 180° Prisms (from alcohol)

METHYL-MALONIC ACID C₄H₀O₄1e CH₃CH(CO₂H)₂ Iso succinic acid Mol w 118 [130°] H C v 365,100 H C p 364,800 H F 218,200 (Stohmann, Kleber, a Langbeir, J pr [2] 40,207) S H (0°-50°) 3372 (Hess P [2] 35,410)

Formation—1 By decomposing a cyano propionic acid with potash (Wichelhaus, Z 1867, 247, Byk, J pr [2] 1, 19)—2 From sodium malonic ether and MeI (Zublin, B 12, 1112)

Preparation—By acting on potassium a bromo propionate with pure aqueous KCy, and saponifying the product by boiling with aqueous

KOH (Cohn, A 251, 335)

Properties — Long prisms or tables (by sublimation) Decomposed on distillation into CO₂ and propionic acid FeCl₃ gives no pp in neutral solutions Fuming HNO, decomposes it into tri nitro ethane, CO₂ and acetic acid (Franchimont, R T C 5, 281) Electrolysis of a concentrated solution of its potassium salt yields hydrogen, CO₂, and oxygen

Salts —NaHA" aq — Na,A"2aq — KHA" —

K,A"aq — CaA" aq — CaA"aq Solubility

Miczynsky (M 7, 269) —BaA" 2aq — ZnA" 3aq

—PbA" aq — Ag,A" heavy granular pp

gradually becoming crystalline

Methyl ether Me₂A" (179°) S G 15 1 107 When treated with HNO₂ (S G 15) it gives a small quantity of CH₂ C(NO₂)(CO₂Me)₂

gives a small quantity of CH, C(NO₂)(CO₂Me)₂

Ethyl ether Et₂A" (1965° cor) (Krestownikoff, B 10, 409), (199°) (Perkin, C J 45, 510) S G ²²/₂ 1021 (Conrad a Bischoff, A 204, 146), 121 10213, 22 10130 (P)

146), \(\frac{1}{8} \) 10213, \(\frac{3}{25} \) 10130 \(\text{P} \) \\ Di-amide \quad \text{CH, CH(CO NH}_2)_2.} \quad [206°]. \\ Formed, together with methyl carbonate, by treating the compound \(\text{CH, C(NO}_2)(\text{CO}_2\text{Me})_2 \) (v \(supra \)) with ammonia (Franchimont, \(R \) T. C. 8, \(286 \)) \(\text{V sl sol alcohol} \)

D1-methyl-d1-amide CH₃CH(CO NHMe)₂ [154°] Formed by the action of methylamine on the ether (Franchimont, R T C 4, 204) Small needles (from benzene), v sol water and alcohol, sl sol ether and benzene Fuming HNO, decomposes it, forming CO, and N,O

Di-methyl-malonic acıd CMe₂(CO₂H)₂. | Isopyrotartaric acid | Mol w | 132 [186°] | H C 515,300 | H F 230,700 (Stohmann, Kleber, a Langbein, J pr [2] 40, 208) | S H (0°-50°) | *310 (Hess, P [2] 35, 410) | Formation — By heating bromo isobutyric scid with KCs and state of the store of the s

acid with KCy and decomposing the resulting nitrile with potash or HClAq (Markownikoff, B 6, 1440, A 182, 324) —2 By boiling di methylbarbituric acid with potash (Conrad a Guthzeit, B 14, 1644) -3 From methyl malonic acid, NaOEt, and MeI (Thorne, C J 39, 543) - 4 By oxidising & acetyl di a methyl propionic acid with nitric acid (3 pts of SG 14 and 1 pt water) (Anschutz, A 247, 105)

Properties -Transparent four sided monoclinic prisms, sl sol alcohol, v sol: water and ether Sublimes in white needles, even at 100° Split up on melting into CO and isobutyric Not attacked by boiling dilute HNO,, and scarcely at all by boiling chromic acid mixture

Salts - Na.A" small efflorescent needles, sl sol water - BaA" stellate groups of thin needles - * CaA" nodules, m sol cold water, deposited on warming its solution - *MgA" crystalline, v sol water — PbA" aq insoluble pp, changing to shining scales on boiling — ZnA" aq S 68 at 24° Monoclinic pyramids (Thorne) — ZnA" 3aq S 94 (Markownikoff) — Ag₂A" small needles, insol water

Ethyl ether Et₂A" (1945°) (Thorne), (1965° cor) (Peikin, C J 45, 511) S G $\frac{35}{49}$ 9965 (T), $\frac{15}{12}$ 1 0015, $\frac{25}{4}$ 9936 (P) M M 9 268 at 14 4°

 $Amide (CH_3)_2C(CONH)_2$ [197°] From the ether and alcoholic NH, at 120° (Thorne)

Amic acid CO₂H CMe₂ CO NH [85°] [85°] A

product of the oxidation of mesitylic acid CH₂ CMe CO₂H

CMe < by KMnO, and H.SO, CO NH

(Pinner, B 15, 580) At 132° it decomposes, giving off CO₂ Boiling KOHA4 forms NH₃ and di methyl malonic acid The potassium salt KA' 2aq crystallises in prisms, v e sol water, m sol alcohol

Di methyl di-amide CMe (CO NHMe), [123°] Long needles (from benzene), v e sol water and alcohol, sl sol ether, m sol benzene (Franchimont, R T C 4, 206) Fuming HNO₃ attacks it, forming N₂O, methyl nitrate, and

dimethylmalonic acid

Tetra methyl di amide CMe₂(CO NMe₂)₂ [80°] (276°) Long prisms (from ligroin), v e sol water, alcohol, and Fuming HNO, forms di methyl benzene malonic acid and di methyl nitramine

DIMETHYL-MALONYL-UREA v DI METHYL-BARBITURIC ACID

METHYL-MANDELIC ACID Methyl derivative of Mandelic acid and Oxy-Tolyl ACETIC ACID

Tetra methyl mandelic acid v Oxy DURYL-ACETIC ACID

METHYL-MELAMINE v Methyl cyanuramide in the article CYANIC ACIDS

METHYL MERCAPTAN CH,S te CH, SH Methyl sulphydrate (5 8°) at 752 mm (Klason, B 20, 3407), (20°) (Gregory, A 15, 239), (21°) (Obermeyer, B 20, 2919) H F p 5,950 H F v 6,370 (Thomsen, Th) Occurs in human

excrement (Nencki, M 10, 863) Obtained by distilling KMeSO, with KHS Prepared by diluting with ice a cold mixture of MeOH (500 c c) and H_2SO_4 (750 c c), adding (2.75 kilos)of) Na₂CO₃ 10aq, and evaporating until most of the Na2SO, has separated The mother liquor is mixed with a solution of potash (500 g) in water (1,000 c c) previously saturated with H2S The mixture is distilled from a water bath, and the gases evolved are passed first through a concentrated aqueous solution of KOH (50 g) and then into a solution of KOH (350 g) in water (700 cc) A small quantity of lead acetate is added to the last solution to ppt H2S, and the methyl mercaptan is then liberated by HCl, dried, and distilled The yield is fair (200 g of MeSH and 40 g of Me₂S) (Klason, B 20, 3407)

Properties -Thin, colourless, highly refrac tive liquid with very repulsive odour

crystalline hydrate

Salts -- Hg(SMe). [175°] Obtained by treating HgO with MeSH, or by passing the gas through an aqueous solution of HgCy2 sol water —Pb(SMe), minute tables —Bi(SMe), minute yellow needles -AgSMe yellow crystalline pp

Reference -Per chloro methyl mercaptan DI - METHYL - MESIDINE C11H1,N $C_pH_{11}NMe_2$ (214°) S G 908 Formed by methylation of mesidine (Hofmann, B 5, 718 Klobbie, R T C 6, 33) By treatment with H₂SO, and HNO₃ (S G 1 5) it is converted into C.Me₃(NO)₂ NMeNO [138°] —B'₂H₂PtCl₂. METHYL METHANE v ETHANE

Di methyl methane v Propane Tri methyl methane v Iso BUTANE Tetra methyl-methane v Pentane PENTAMETHENYL METHYL

TRIHY. DRIDE DICARBOXYLIC ACID C,H10O, 16. CO H CH<CH $^{\circ}$ CH $^{\circ}$ >C CO $^{\circ}$ H [188°]

tained by saponifying its ether which is among the products resulting from the distillation of di methyl butylene diketone dicarboxylic (di acetyl adipic) ether with KOH (Perkin, jun, C J 57, 227, 233) Glistening needles or groups of plates, v sol hot water, alcohol, and acetone. sl sol cold light petroleum, benzene, CS2, and chloroform

Reactions —1 Its aqueous solution decolour ises bromine in the cold and on evaporating to a syrup it gives off HBr -2 HBrAq in sealed tubes at 110° forms C₆H₁₁Br, a light brown oil, probably bromo methylpentamethylene -3 Sodium-amalgam has no action

Salts — $\times (NH_4)A''$ gelatinous — Ag_2A'' : heavy white pp which darkens in daylight — Salts -- *(NH,)A" AgHA" slender needles, v sol hot water

METHYL PENTAMETHENYLYL METHYL KETONE TRIHYDRIDE C.H., O te

CH. CMe CH₂< Methyl dihydropentens ·CH., Č CO CH,

methyl ketone (191°) Formed by the action of boiling alcoholic potash on di-methyl butylene diketone dicarboxylic (di acetyl adipic) ether (Marshall a Perkin, jun, C J 57, 232, 244) Colourless mobile oil, smelling like peppermint Lighter than water V sol alcohol and ether Readily reacts with phenyl hydrazine. May be

reduced to the alcohol C, H, O, whence HI at |

250° yields C_8H_{16} Oxim $C_8H_{12}(NOH)$ [85°] Formed by the action of hydroxylamine hydrochloride on the ketone dissolved in methyl alcohol colourless prisms, v sol alcohol, ether, acids, and alkalis May be distilled with slight de composition — (C₈H₁₃NO)₂H₂PtCl₆ tufts of orange crystals, v sol boiling alcohol, decomposing at 192°

METHYL METHRONIC ACID C.H 100, 1.e. CH(CH₃) CH CO₂H

·C(CO₂H) CMe CH_2 — $C(CH_3)$ CO_2H CO

Dr methyl keto-C(CO,H) CMe

pentene dicarboxylic acid [198°] Formed by heating acetoacetic ether, sodium pyruvate, and Ac₂O at 140°, and saponifying the resulting ether with baryta or NaOH (Fittig, A 250, 195) White needles, v sol HOAc, ether, hot alcohol, and hot water, sl sol cold water, CS2, and benz ene, almost insol petroleum ether At 250° it 18 split up into CO_2 and methyl uvic acid $C_8H_{10}O_7$ [98°], which on prolonged boiling yields СН(СН.) СН. CH CH CH,

or CO _CMe CH_ CH=CMe oil, boiling at 119°

Salts - BaA' 2aq small needles, v e sol water - CaA" 3aq small prisms - Ag A" silky

nodules, sl sol water

Mono-ethyl ether EtHA" Obtained by boiling the di ethyl ether with alcoholic potash Yellow syrup, sl sol water—Ba(EtA"), aq yellow gummy pp, v e sol water and alcohol -Ca(EtA"), 2aq needles, m sol water, v sol hot alcohol -AgEtA" flocculent pp, sl sol water, v sol alcohol and ether

D2-ethyl ether Et₂A" (280° un Heavy oil, miscible with alcohol and ether (280° uncor)

METHYL TETRAMETHYLENE C.H., 1e $CH_2 < CH_2 > CHMe$ (c 40°) Formed by the action of sodium on as di bromo pentane dis solved in toluene (Colman a Perkin, C J 53,

Very volatile oil Does not combine with conc HIAq METHÝL PENTAMETHYLENE CeH12 1 e

CH₂ CH₂ CHMe? Formed by the action of finely divided sodium on as di bromo hexane dis solved in toluene (Perkin, C J 53, 214) not attacked by HI

METHYL - PENTAMETHYLENE CARB. OXYLIC ACID C,H,2O, 1 e

CH, CHMe CH (220°) SG # 10205, CH, CH CO,H

20 1 0174, 25 1 0144 MM 6 914 Formed by heating methyl pentamethylene dicarboxylic acid a little above its melting point (Colman a Per-kin, jun, C J 53, 194) Colourless oil. Bromine at 110° attacks it with evolution of HBr-BaA'₂ syrup—AgA'' white amorphous pp

Methyl-pentamethylene dicarboxylic acid CH, CHMe

. [175°] Ob-O.H.,O. i.e CH₂ C(CO₂H)₂ tained by boiling its ether with alcoholic potash

(C a P) Prisms (from ether), or plates (from water), v sol alcohol, ether, and hot water, m. sol cold water —Ag, A' white pp

Ethyl ether Et₂A" (244°) Obtained from CH₂ CHBr CH₂ CH₂ CH₂Br, malonic ether and NaOEt Thick oil

METHYL - HEXAMETHYLENE CARB-OXYLIC ACID C,H14O, 1e

CH₂ CH₂ CHMe CH CO₂H o Toluic acid MM .7 975 For (236°) hexahydride? 1 0033, 20 9966 Formed by decomposing the dicarboxylic acid by heat (Per kin, jun, C J 53, 208, 213) It is also one of the products of the electrolysis of methyl hexa methylenyl methyl ketone carboxylic ether by alcoholic potash Colourless oil -AgA whitepp.

Methyl hexamethylene dicarboxylic acid C₂H₁₄O₄ te CH₂CH₂CH₂CH₄ >C(CO₂H)₂ [147°].
Obtained by hydrolysing its ether with alcoholic potash (Perkin, C J 53, 207) Crystalline pow der, v sol ether, alcohol, and hot water, sl sol cold water -Ag2A" white amorphous pp

Ethyl ether Et.A" (c 263°) Obtained from CH, CHBr CH, CH, CH, CH, Br, malonic ether, and NaOEt (Perkin, jun, C J 53, 206) Thick oil, with unpleasant odour

METHYL TETRAMETHYLENE KETONE v. TETRAMETHYLENYL METHYL KETONE

METHYL - TRI METHYLENE CARBOXYLIC ACID v TRI METHYLFNYL MFTHYL RETONE CARBOXYLIC ACID

METHYL PENTAMETHYLENE METHYL KETONE v METHYL PENTAMETHYLENYL METHYL

TETRA-METHYL-v-TRIMETHYLENE-DI-PYRROLE C15H22N2 1 e CMe CH HC CMe >N C₃H₅ N∢ [77°] Formed

HC CMe CMe CH by heating acetonyl acetone (2 mols) and tri methylene diamine (1 mol) in conc alcoholic solution at 120° Crystalline solid Sol alco hol and ether, insol water (Paal a Schneider, B

DI METHYL-TRI METHYLENE TRI SUL-PHONE C₃H₄(CH₃)₂S₃O₆ [330°-340°] bodies of this formula are produced when 1 g tri methylene tri sulphone in 10 cc of 5 pc caustic soda is heated with an equal volume of methyl iodide These two substances crystallise together in glittering needles By further methylation the hexamethyl derivative is formed (E Baumann a R Camps, B 23, 72)

Tetra methyl dı methylene dısulphone

 $CMe_2 < SO_2 > CMe_2$ Di isopropylidene di sul [220°-225°] phoneObtained from acetone (1 pt) by heating it with P₂S₃ (1 pt) at 125° for 7 hours, distilling with steam, and oxidising the resulting 'duplo'-thio acetone S₂(CMe₂), with KMnO₄ (Autenrieth, B 20, 373) Slender white KMnO, (Autenrieth, B 20, 373) needles, v sol alcohol and ether, sl sol hot water Not attacked by HNO₃ and H₂SO₄, nor by boiling dilute aqueous KOH

METHYL PENTAMETHYLENYL METHYL. CARBINOL C.H.O 1 e

CH, CHMe CH CH(OH) CH, (180°) Ob-CH. CH.

tained by reducing the corresponding ketone in ethereal solution with sodium (Marshall a Perkin, jun, C J 57, 247) Colourless liquid, with strong odour of menthol, sl sol water, v sol alcohol and ether On boiling with Ac₂O it yields a strongly refracting acetyl derivative with agreeable odour Excess of solution of hydriodic acid (S G 196) forms a heavy oily iodide CH₂ CHMe.

CH, CH, CH, (155°-160° at 90 mm),

which smells like see hexyl iodide, and is slightly decomposed on distillation

METHYL-HEXAMETHYLENYL METHYL-CARBINOL $C_0H_{10}O$ i e

CH₂CH₂CHMe CH.CH(OH) CH₂ Hexahydrade of a tolyl methyl carbinol (195°-200°) Formed by reducing tetrahydro tolyl methyl ketone in ethereal solution with sodium (Kipping a Perkin, jun, C J 57, 22) Thick, colourless liquid, smelling like menthol, all sol water, miscible in alcohol and ether When mixed with cone HIAq it dissolves with evolution of heat and separation of the corresponding todice

METHYL-PENTAMETHYLENYL METHYL

KETONE C.H.O te CH.

CH, CH CO CH, (171°) S G 4 9222, 10 9174, 15 9136, 25 9970 M M 8 01°) Obtained as one of the products of the hydrolysis of its carboxylic ether by alcoholic potash (Colman a Perkin, C J 53, 198) Colourless oil, smelling of peppermint Readily combines with phenyl hydrazine and with hydroxylamine Dissolves with difficulty in a solution of NaHSO₃

Methyl-hexamethylenyl methyl ketone

CH₂CH, CHMe>CH CO CH, o Tolyl methyl ketone headhydride (198°) Obtained as one of the products of the hydrolysis of its carb oxylic ether by alcoholic potash (Perkin, C J 53, 213) Colourless oil, smelling, when in small quantities like new mown hay

METHYL TRIMETHYLENYL METHYL KETONE CARBOXYLIC ACID C,H₁₀O, 1 & CHMe.

Propylene aceto

C(CO₂H) CO CH₃

CH₂

acetic acid Obtained by saponifying its ether, which is produced by treating acetoacetic ether with NaOEt and propylene bromide (Perkin, jun, B 17, 1443) Thick oil, splitting off CO₂ when heated—AgA' amorphous powder, sl sol water

Ethylether Eth (210°-215°) at 720 mm Methyl-pentamethylenyl methyl ketone CH₂ CHMe

carboxylic ether CH₂ CH₂ C(CO₂Et) CO CH₃ (238°) Obtained by the action of a5 di bromo pentane on sodium aceto aceto ether (Colman a Perkin, jun, C J 53, 197) Thick, colourless oil On hydrolysis with alcoholic potash it yields the corresponding ketone as well as the

Methyl-hexamethylenyl methyl ketone carboxylic ether

CH₂ CH₂ CHMe C(CO₂Et) CO CH₄. Hexa

METHYL-MORPHINE v Cedeine

(a) METHYL-NAPHTHALENE $C_{11}H_{10}$ 2 ε $C_{\varepsilon}H$ C_{H} C_{H}

(S), (232°) (F a R) SG $^{11.5}$ 1029 Occurs, together with (β) methyl naphthalene, in the fraction of coal-tar oil boiling between 200° and

300° (Schulze, B 17, 844)

Formation—1 By the action of sodium on a mixture of MeI and (a) brome naphthalene (Fittig a Remsen, A 155, 114)—2 By distilling colophony, gum benzoin, or aldehyde resin with zinc-dust (Ciamician, B 11, 269, M 1, 193)—3 By distilling (a)-naphthyl acetic acid with lime (Boessneck, B 16, 1546)

Properties — Colourless liquid, not solid at —18° Boiling cone HNO, oxidises it to (a)

naphthoic acid

Picric acid compound

C₁₁H₁₀C₆H₂(NO₂)₃OH [117°] Long, slender orange needles (from alcohol)

(β) - Methyl - naphthalene $C_{10}H$ (CH_{2}) ie CH CMe $C_{2}H$ ($CH_{2}H$ $C_{3}H$ $C_{4}H$ $C_{4}H$

the fraction of coal tar oils boiling at $200^{\circ}-300^{\circ}$. The oil is shaken with NaOH and with H_2SO_{\bullet} to remove phenols and bases, and fractionally distilled. By cooling the fraction $239^{\circ}-242^{\circ}$ to 0° . the (β) methyl naphthalene separates out, leaving the liquid (a) methyl naphthalene (Schulze, B 17, 842, 1203, Reingruber, A 206, 367). Could not be obtained from (β) bromo naphthalene MeI and Na (Brunel, B 17, 1179). White plates, insol water, sol alcohol, ether, and benzene, volatile with steam. Completely decomposed on oxidation. Yields, on chlorination at 245° , C_{10} H CH₂Cl [47°]

Picric acid compound [115°], yellow needles

D1-methyl-naphthalene C12H12 te C16H6Me2. (110° at 6 mm), (c 265°) at 760 mm S G 6 10283, 13 10199 (C a C), 22 10176 (G), 164 10180 (Nasını, G 15, 84) R∞ 87 25 (N)

Formation —1 From di bromo naphthalene

Formation—1 From di bromo naphthalene [81°], sodium, and MeI (Mono, B 13, 1517)—2 By heating santonin, or the dimethyl naphthol derived therefrom, to redness with zinc dust (Cannizzaro a Carnelutti, G 12, 410)—3 By heating dimethyl naphthol hydride with sulphide of phosphorus (Cannizzaro, G 13, 393)

Preparation—D1 bromo naphthalene dissolved in toluene is heated with MeI and sodium, the product is heated to 150° to remove MeI and toluene, and the residue extracted with ether. The extract is fractionally distilled, and the fraction 260°-270°, after rectification under 12 mm pressure, is heated with sodium at 100° to remove any unaltered di bromo naphthalene. The di methyl naphthalene is finally obtained pure by means of its compound with pieric acid (Grovanozzi, G 12, 147)

Properties - Colourless, highly refractive oil, not solid at -18° With bromine it appears to form C12H12Br, and C12H9Br,

Picric acid compound [189°] Orange

needles, sol alcohol and ether

Hexahydride C12H18 SG 194 922 Ro 86 14 (Nasını a Bornheimer, G 15, 93) Formed by treating the di methyl naphthalene with HIAq and phosphorus (Zuco, G 15, 81)

Di-methyl-naphthalene $C_{12}H_{12}$ (265°) curs in coal tar (Emmert a Reingruber, A 211, 365) Not solid above -18°

Pecric acid compound C₁₂H₁₂C₆H₂(NO₂)₃OH [118°] Orange prisms Trimethyl-naphthalene C₁₃H₁₄ i e C₁₀H₅Me₃ (275°) Obtained (according to Maschke, C C 1886, 824) by heating di methyl-(\$\beta\$) naphthylamine methylo iodide at 320°, and distilling the resinous product with steam

Picric acid compound [133°]

References - Bromo- and Chloro METHYL-NAPHTHALENLS

(a)-METHYL-NAPHTHALENE SULPHONIC ACID C10H8Me SO3H Obtained by sulphonating (a) methyl naphthalene (Fittig a Remsen, A 155, 115) -BaA'2 sl sol water

(β)-Methyl-naphthalene sulphonic acid C₁₀H_eMe SO₃H Obtained by sulphonating (β)methyl naphthalene (Reingruber, A 206, 377) Syrup -BaA'2 amorphous mass

Di-methyl-naphthalene sulphonic acid C₁₀H₂Me₂SO₃H Obtained by the action of HSO₄ at 120° on the di-methyl naphthalene derived from di bromo naphthalene [81°] (Giovanozzi, G 12, 147) Deliquescent scales — KA'aq ırıdescent lamınæ

Di-methyl-naphthalene sulphonic acid C10H5Me2 SO3H Obtained by heating the dimethyl naphthalene of coal tar with fuming H₄SO₄ (Emmert a Reingruber, A 211, 365) *BaA'2 sl sol water

Di-methyl-naphthalene di-sulphonic acid C₁₆H₄Me₂(SO₃H)₂ Formed at the same time as the preceding, from which it differs in having an easily soluble barium salt (E a R)

METHYL-NAPHTHAQUINOLINE V METHYL-NAPHTHOQUINOLINE

(In 2) METHYL (a)-NAPHTHINDOLE C13H11N & C C10H6 CH [132°]

tained by heating (1 pt of) the (a) naphthyl hydrazide of acetone with ZnCl₂ (2 pts) at 180° (Schlieper, A 239, 237) Slender needles (from water), v sol alcohol and ether Colours pine wood, acidified by HCl, bluish violet FeCl, imparts a cherry red colour to its solution in HOAc, and on adding water a pp is formed

Picrate [168°], dark red needles (from hot

benzene)

 $(In \ 2)$ -Methyl- (β) -naphthindole

 $C_{10}H_{e}$ < $\stackrel{CH}{\sim}$ > CMe (314°-320° at 223 mm) Prepared by heating the (β) naphthyl hydrazide of acetone with ZnCl₂ at 175°, dissolving the fused mass in water, and extracting with ether (Schlieper, A 236, 182) Liquid, v sl sol water, v sol alcohol, ether, and benzene Colours acidified pine-wood violet NaNO2 added to the

acetic acid solution gives a brown pp
Picrate [176°]; reddish brown needles

(from hot benzene).

DihydrideC13H13Nie C10H4 CHH. CHMe.

(190°-200° at 20 mm) Obtained by treating me thyl (β) naphthindole with zinc dust and HClAq, until it ceases to give the pine wood reaction, then adding NaOH and extracting with ether Yellow oil, which in an ethereal solution ex hibits blue fluorescence Forms soluble crystalline salts with mineral acids Reduces AgNO, on warming Gives an oily nitrosamine

(In 1, 2)-D1-methyl (a) naphthindole C14H13N e C₁₀H₆<NH CMe [150^] Formed by heat ing bromo acetyl propionic (bromo levulic) acid CH, CO CHBr CH, CO, H (2 pts) with (a) naph thylamine (7 pts) (Wolff, B 21, 3365) White White granules or prisms (from alcohol), v sol ether and benzene, m sol cold alcohol and HOAc, insol water Its solution in conc HClAq is ppd by water FeCl_s colours its solution in HOAc cherry red, whilst K2Cr2O, give a deep blue

(In 1, 2) Di-methyl-(8)-naphthindole

360°) Prepared by the action of bromo acetyl propionic acid on (8) naphthylamine (Wolff, B21, 3363) Plates (from alcohol), v e sol ether and benzene, m sol cold alcohol and HOAc, insol water FeCl, colours its solution in boil The concentrated alcoholic ing HOAc green solution exhibits violet fluorescence

Picrate [175°], dark brown needles (In 1, 2)-Di-methyl- (β) -naphthindole

C₁₀H₆ CMe CMe [126°] Possibly identi cal with the preceding body Formed by heat ing (In 1, 2) methyl (3) naphthindyl acetic acid at 210° (E Fischer a Steche, A 242, 370) Six sided plates, insol water, v sol alcohol and HOAc FeCl, gives a blue colouration to its solution in HOAc Yields a crystalline nitios amine Reacts with MeI forming di methyl (B)naphtho quinoline dihydiide

Picrate dark red crystals Dihydride C, H, Nie

C₁₀H₆ CHMe Obtained by reducing the di methyl (3) napthindole with zinc-dust and HCl Oil, turning red on oxidation Forms a crystalline platinochloride, decomposed by boiling water

(In 1, 2)-METHYL- (β) NAPHTHINDYL ACETIC ACID C15H13NO2 1 e

 $C_{10}H_{6} < \begin{array}{c} CMe \\ NH \end{array} > C CH_{2} CO_{2}H \quad [210^{\circ}] \quad \textit{Di methyl}$ naphthindole a-carboxylic acid Formed by heating the (3) naphthyl hydrazide of 3 acetylpropionic ether with ZnCl₂ at 135° (Steche, A 242, 368) Small crystals containing 1C,H,O (from acetone), v sl sol water, benzene, and chloroform, v sol alcohol, ether, acetone, and Loses CO₂ on heating —AgA' white pp which yields a silver mirror on boiling with water

METHYL-NAPHTHOCOUMARIN v Anhydride of Oxy-naphthyl crotonic acid

METHYL-(a) NAPHTHOFURFURANE

O₁₂H₁₀O 2 e O₂H CH C CMe CH [35°]

(298°) Obtained by distilling its carboxylic and alone or with KOH (Hantzsch a Pfeiffer, B 19, 1304) Very volatile with steam Reduces AgNO, on boiling Its solution in H.SO, becomes green, and finally violet, on warming, on dilution with water it becomes green again

Methyl (\$) naphthofurfurane

by distilling its carboxylic acid alone or with soda lime (H a P) Resembles the preceding isomeride

METHYL - (α) - NAPHTHOFURFURANE CARBOXYLIC ACID $C_{14}H_{16}O_{3}$ 2 σ

the action of chloro aceto acetic ether on sodium (a) - naphthol there is formed $C_{10}H_{\gamma}O$ CHAc CO₂Et, and this ether is then mixed with H₂SO₄, and the product poured into water The ppd ethei is then saponified by alcoholic potash (Hantzsch a Pfeiffer, B 19, 1301) Needles (from HOAc), which may be sublimed, v sl sol alcohol and ether, almost insol water

Ethylether EtA' [109°] Flat needles (from alcohol), v sol ether and hot alcohol

Methyl- (β) -naphthofurfurane carboxylic acid

in the same manner as the preceding isomeride, which it greatly resembles, by using sodium (\$\beta\$)-naphthol (H a P)—NaA'4aq blue fluorescent needles

(β) METHYL (α) NAPHTHOL

C₁₁H₁₀O i e C₁₈H₂Me OH [89°] Formed as by product, together with phenyl butylene, by distilling (a) phenyl methyl paracomo acid C₈H₃ CH CH(CO₂H) CHMe CO (Fitting a. L.

Liebmann, A 255, 263) Long slender elastic needles, v sl sol water FeCl, gives a white pp Bleaching powder produces a green pp which becomes yellow On distillation with zinc dust (3) methyl naphthalene is formed

(β)-Methyl-(a) naphthol C₁₀H₄Me OH [92°] Formed by distilling (β)-phenyl methyl para come acid (Fittig a Liebmann, A 255, 272) Long elastic white needles (from boiling water), volatile with steam FeCl, gives a white pp which becomes yellow on standing Bleaching powder forms a green pp, quickly becoming yellow On distillation with zinc-dust it yields (β) methyl naphthalene

Di methyl naphthol CieH.Mer.OH [136°]
Obtained by heating santonous or isosantonous acid with Ba(OH), above 360° The product is dissolved in water, and on passing CO, through the solution di-methyl naphthol is ppd together with BaCO₃, which is removed by HClAq (Cannizzaro a Carnelutti, G 12, 406) Glisten ing needles (from alcohol), v sl sol water, sol alcohol and ether Begins to sublime at 100°

Chromic acid in HOAc exidises it to $C_{12}H_{12}O_{2}$ crystallising in tables $[105^\circ]$, which may be reduced to di methyl naphthol by HI and phosphorus On heating to redness with zinc dust it yields di methyl naphthalene identical with that obtained from di bromo naphthalene [81°]

that obtained from di bromo naphthalene [81°]

Methylether C₁₂H₁₁ OMe [68°] Prisms,
sol alcohol and ether

Ethyl ether C₁₂H₁₁ OEt Viscid liquid Acetyl derivative C₁₂H₁₁ OAc [78°]. Lamine

Dihydride C₁₂H₁₄O [113°] Obtained by saponification of its propionyl derivative, which is one of the products of the dry distillation of santonous acid Separated from accompanying di methyl naphthol by frequent crystallisation from light petroleum (Cannizzaro, G 13, 390) Glistening white needles, v sol ether and alcohol, insol water Volatile with steam P₂S₃ converts it into di methyl naphthalene

(Py 3) METHYL-(a) NAPHTHOQUINOLINE

CH CH

a | a Naphthoquinaldine (above

300°) Heavy liquid Formed by heating (a) naphthylamine with paraldehyde and HCl Its salts have a blue fluorescence in dilute solution—B'₂H₂Cl₂PtCl₄2aq concentric needles—B'₂H₂Cr₂O, yellow crystals (Doebner a Miller, B 17, 1711)

(Py 1) Methyl (β) naphthoquinoline C₁₄H₁₁N

with (β) naphtho acridine and a base $C_{24}H_{20}N_{2}$, by the action of a mixture of methylal, acetone, and HCl upon (β) naphthylamine (Reed, J pr [2] 35, 316)—Picrate BC₆H₂(NO₂)₃OH

(Py 3) Methyl-(β)-naphthoquinoline

(above 300°) Formed by heating (3) naphthylamine with paraldehyde and HCl (Doebner a Miller, B 17, 1711, Seitz, B 22, 254) Large colourless needles V sol alcohol and ether, al sol water With chloral it forms a crystalline compound C₁₃H₈N CH₂ CH(OH) CCl₃ [185°]

Salts—B'₂H Cl PtCl₄2aq yellow, sparingly soluble needles — B'.H Cr.O small needles, sl sol hot water —B'HCl 2aq slender needles, sl sol cold water —B'HNO₄ aq slender needles, becoming rose coloured in B'H₂SO₄ 2aq very slender needles, v e sol hot water —B'C,H (NO₂)₃OH [221°] Minute needles, v sl sol boiling water, v sol HOAc

Methylo rodide B'MeI [241°-247°]. Straw coloured needles, v sol boiling water, sl. sol alcohol

(Py 3) Methyl-(β)-naphthoquinoline

C₁₀H₆CH CH [92°] Possibly identical with

the preceding isomeride Formed by heating (Py 1, 3) oxy methyl naphthoquinoline to redness with zinc-dust (Knorr, B 17, 544) Crystal line May be distilled Its acid solutions fluoresce blue when dilute, green when concentrated—B'₂H₂PtCl₄ al. sol hot dilute HClAq.

(Py 1, 3) Di-methyl-(a)-naphthoquinoline CMe CH −Č N == CMe te. C.H. N=CMe `СН СН Ё СМе ĊН [44°] (361°) Formed by heating at 100° a mixture of (a)-naphthylamine with ethylidene-acetone, de rived from acetone and paraldehyde (Reed, J pr [2] 35,312) Formed also by heating (a)-naphthylamine (1 mol) with acetyl-acetone (1 mol), and heating the product with H2SO, at 100° (Combes, C R 106, 1536) Needles (from petroleumether), v e sol ether, insol 90 pc alcohol Somewhat volatile with steam Its solution in H₂SO₄ is coloured purple by K₂Cr₂O₇ solutions of its salts fluoresce violet (C) hydrated platinochloride is violet, after drying en vacuo it melts at 260° (C) —B'C, H2(NO2)3OH [223°] Needles

 $(\bar{P}y = 1, 3)$ -Di methyl (β) naphthoquinoline

C₁₅H₁₅N to C₁₀H₆CMe CH N CMe ___C CMe CH CH CH CN CMe [127°] (above 300°)

Formed from (B) naphthylamine hydrochloride by heating at 100° with ethylidene acetone, the product of the condensation of paraldehyde with acetone in presence of hydrochloric acid, as follows C₁₀H₂NH₂+Me CO CH CHMe = C₁₃H₁₃N + H₂O + H₂ (Reed, J pr [2] 35, 299) Flat needles (from ether), v sl sol boiling water, hardly volatile with steam KMnO₄ oxidises it to (8) di methyl phenyl pyridine dicarboxylic acid

It does not yield a nitrosamine

Salts—Picrate B'C₆H₂(NO₂)₂0H [215°]

— B'H₂Cr₂O₇ [c 115°] — B'₂H₂PtCl₆ 2¹aq —

B'H₂SO₄—B'HNO₈ [181°]—B'₄HBr₅ [207°]—

B'HBr 2aq

Methylo vodide B'MeI needles Sulphonic acid C15H12(SO3H)N 12aq minute needles, insol water and alcohol

Disulphonic acid C₁₅H₁₁(SO₃H),N 4¹aq needles, v e sol water and alcohol—CuH₂A''₂5aq—BaA'' 7aq Potash fusion produces C₁₅H₁₁(OH)(SO₃H)N Potash fusion pro-

Di-methyl (3) naphthoquinoline C,,H,,N [67°] (380°) Obtained by heating (3) naphthyl amine with acetyl acetone and H2SO, at 100° (Combes, C R 106, 1537) Its yellow sulphonic acid C15H13NSO3 is also ppd on adding ammonia to the aqueous extract of the product The base forms a greenish yellow platinochloride, decomposing at 220° without melting

DI-METHYL-(A)-NAPHTHOQUINOLINE DI-

CMe CMe HYDRIDE C15H15N 2 e C10He [115°] NH CH,

Formed by heating (In 1, 2) di-methyl (β) naphthindole with MeI in sealed tubes for 15 hours at 100° (Fischer a Steche, B 20, 820, A 242, 364) Plates, v sl sol water, v sol ether, alcohol, and mineral acids, volatile with steam With nitrous acid it yields a crystalline nitros amine -B'HI Needles (from water), sl sol water and alcohol -The platinochloride is sl sol water and alcohol

METHYL NAPHTHYLAMINE v NAPHTHYL-

METHYL AMINE

Methyl di naphthyl-amine v. Di-NAPHTHYL METHYL-AMINE.

DI-METHYL-NAPHTHYLENE DIAMIN & ...

NAPHTHYLENE DI-METHYL DI AMINE METHYL-NARCEINE v NARCEINE

METHYL-NARINGENIC ACID v Methy!

derivative of p Coumaric acid METHYL-NICOTINE v NICOTINE

METHYL-NICOTINIC ACID v METHYL-

PYRIDINE CARBOXYLIC ACID
METHYL-NITRAMINE v METHYLAMINE

METHYL NITRATE CH, NO, te CH, O NO, Mol w 77 (65°) S G 1 12167, 23 1 2032 M M 2 057 (Perkin, C J 55, 682) S V 69 3 (Lossen, A 254, 73) Obtained, together with methyl nitrite, by distilling wood spirit with NaNO, and H₂SO, (Dumas a Péligot, A Ch [2] 58, 37) Prepared by distilling methyl alcohol (200 cc) with urea nitrate (40 g) and HNO₃ (150c c of S G 1 31) free from nitrous acid When two thirds have passed over, an additional quantity of MeOH (170 cc) and HNO, (110 cc) may be added and the distillation continued (Carey Lea, Am S [2] 33, 227) The process may also be conducted in a continuous manner (v LTHYL NITRATE)

Properties - Colourless liquid, exploding when struck or when its vapour is heated solid KOH it yields Me₂O (Berthelot, A 113, 80) When diluted with MeOH (4 vol) and treated with a current of gaseous NH, it gives methylamine nitrate and NMe, NO, with only traces of dı and trı methylamine Aqueous ammonia forms NMeH₂ (13 pts), NMe₄NO₈ (10 pts), and a small quantity (1 pt) of the bases NMe.H and NMe, (Duvillier a Malbot, A Ch [6] 10, 281)

METHYL NITRITE CH, NO, 1 e CH, O NO Mol w 61 (-12°) S G (liquid) - 991 Produced by treating methyl alcohol with nitric acid and copper turnings or arsenious acid (Strecker, C \bar{R} 39, 53, A 91, 82) The product is passed through a receiver at 0° and the gas after purification by passing through potash, a solution of ferrous sulphate, and div CaCl, is condensed at -40° It may also be prepared from methyl alcohol, NaNO, and H,SO,

Properties -Gas, smelling like nitrous ether

Burns with a green edged flame

METHYL NITRO-AMIDE v METHYLAMINE METHYL - NITRO - ANILINE METHYL ANILINE

METHYL NITRO-BENZAMIDE v Amide of NITRO TOLUIO ACID

METHYL-NITROLIC ACID CH N O. 2 e CH(NO₂) NOH or CH₂(NO₂)(NO) Mol w 90 Prepared by dissolving nitro methane $[64^{\circ}]$ (15 g) in water, adding a solution of $KNO_2(8 g)$, cooling to 0°, and adding a very dilute ice cold solution of H₂SO₄ (4 g) Caustic potash solution is added till the liquid turns red, and then more dilute H,SO, The liquid is then shaken with a little CaCO, and extracted with ether (Tscherniak, B 8, 114, A 180, 166) The result is very uncertain (V Meyer a Constam, A 214, 335)

Properties —Long needles (from ether) composes slowly in the cold, rapidly at 64°, into formic acid, NO₂, and nitrogen By boiling dilute H.SO, it is resolved into formic acid and N₂O Sodium amalgam reduces it to methylazaurolic acid CH(NOH) N N CH NOH amorphous powder which is violently gasified above 100°.

DI-METHYL-NITROSAMINE v DI METHYL-AMINE

METHYL NITROSO-ETHYL KETONE v. Mono oxim of DI-METHYL DIRETONE

TETRA METHYL-NITROSO-PHENYLENE-DIAMINE v NITROSO-PHENYLENE TETRA METHYL DIAMINE

METHYL NONYL RETONE v METHYL ENNYL KETONE

METHYL-NOROPIANIC ACID v OPIANIC

METHYL n OCTYL KETONE C. H.O 16 CH₃ CO CH₂ CH₂ CH₂ CH₂ CH₂ CH₂ CH₃ CH₃ [4°] (214°) (J), (211°) (K) $\overset{\circ}{\text{S}} \overset{\circ}{\text{G}} \overset{176}{_{175}} 8294$, 1 838, 20 825 (K) Formed by boiling heptylaceto acetic ether with dilute alkalis (Jourdain, A 200, 106) Formed also by distilling a mixture of barium acetate and barium ennoate (Krafft, B 15, 1695) Liquid, with pleasant odour, insol water, solidifying in a freezing Forms a crystalline compound with NaHSO,

Methyl octyl ketone C10H20 1 e

CH, CO CH. CHMe C,H, Heptyl acetone (197°) Formed by the action of baryta water on n sec heptyl aceto acetic ether (Venable, B 13, Colourless liquid, lighter than water 1651)

METHYL OCTYL OXIDE C,H20 1 e CH₃ O C₈H₁₇ (173°) S G ⁶ 8014 S V 219 8 C E (0°-10°) 00101 (Dobriner, A 243, 3)

METHYL OCTYL PHENYL AMINE V OCTYL TOLYL AMINE

METHYL-OCTYL-THIOPHENE $C_{13}H \ S \ \imath \ e$ $s <_{C(C_8H_1)}^{CMe} \xrightarrow{CH} >$ [10°] (272°) Formed by the action of sodium upon an ethereal solution either of MeI and iodo octyl thiophene or of octyl bromide and 10do methyl thiophene (Schweinitz, B 19, 648) Bromine forms C18H. BrS 2001

METHYL OXALATE v Methyl ether of OXALIC ACID

METHYL-OXALACETIC ETHER C.H.O. 1 e CO Lt CO CHMe CO Et Oxaloxyl propionic (138° at 23 mm) Formed by the action of NaOEt on an ethereal solution of oxalic and propionic ethers (Wislicenus a Arnold, B 20 3394, A 246, 329) Formed also from sodium oxalacetic ether and MeI at 100° Colouiless oil, v sol alcohol and ether Its alcoholic solu tion gives a red colouration with FeCl, Split up by boiling alcoholic potash into oxalic and pro pionic acids Boiling dilute H.SO, yields ethyl glyoxylic acid

Salt -CO,Et CO CNaMe CO,Et Does not crystallise from alcohol

Phenyl hydraside CO Et C(N,HPh) CHMe CO.Et [100°] Small plates, v sol ether and benzene Its solution in conc H.SO, is coloured reddish violet by FeCl. At 120° it gives off alcohol, forming a derivative of pyrazole

METHYL-OXALYL UREA v PARABANIC ACID METHYL-OXAMIC ACID v OXALIC ACID METHYL-OXAMIDE v OXALIC ACID METHYL-OXANTHRANOL v OXANTHRANOL METHYL-OXAZOLE DIHYDRIDE C.H,NO CH, O CMe. Formed, in small quantity, OH.N/

by the action of Ac,O and NaOAc on bromoethylamine Br CH, CH NH, (Gabriel, B 22, 2221, 23, 2502) Oil, with sweet smell, somewhat like quinoline $-B'C_6H_2(NO_2)_3OH$ [149°]. Yellow plates.

METHYL-OXETHYL- v METHYL-OXYETHYL-DI-METHYL-OXETONE v Anhydride of Di-7-0XY-DI-BUTYL DIRETONE

DI-METHYL OXIDE C.H.O re (CH.).O Methyl ether Mol w 46 (-24°) (Regnault, J 1863, 70) V D 1617 S (gas) 37 at 18° H F p 49,640 (Thomsen), 56,800 (Berthelot, A Ch [5] 23, 185) HF v 48,190 (T) HCp 344,200 (B) Formed by heating MeOH with H.SO. (Dumas a Peligot, A 15, 12, Kane, A 19, 166) or with B.O. (Ebelmen, A 57, 328) Formed also, together with NMe, Cl and NMe, HCl, by heating NH Cl with excess of MeOH (Weith, B 8, 458) Prepared by heating MeOH (13 pts) with H_2SO_4 (20 pts) at 140° The gas is passed through aqueous KOH to remove SO2, CO2, and MeOH, and then into conc HSO, which absorbs 600 vols It is obtained by dropping the solu tion in H2SO, into an equal volume of warm boiled water, and is dried by passing through tubes containing CaCl₂ (Erlenmeyer a Kriech baumer, B 7, 699, cf Tellier, Ar Ph [3] 10,

Properties - Gas Combines with HCl form ing Me OHCl which boils at 2°

References - Chloro and DI 1000 DI METHYL

METHYL - OXINDOLE C.H.NO C.H. CH. CO Oxy methyl indole [88°]

Obtained from methyl indole carboxylic acid by the action of NaOBr, the resulting di biomo methyl oxindole being suspended in alcohol and reduced by sodium amalgam (Colman, C J 55, 7, A 248, 120) White needles, sl sol cold water and light petroleum, v sol alcohol, ether, acetone and benzene Dissolves in hot alkalis without change Partially decomposes when heated much above its melting point Does not react with phenvl hydrazine Bromine water gives a crystalline pp Nitrous acid conveits it into C.H. C(NOH) CO, the oxim of methyl ψ isatin

Di-chloro methyl oxindole $C_8H_4 < \frac{CCl}{NMe} > CO$. [147°] Formed by adding a solution of sodium methyl indole carboxylate to a cold solution of NaOCl (Colman) Colourless needles, v sol hot alcohol and acetone, m sol ether Not decom

posed at 210 Bromo methyl oxindole C,H,CHBr>CO

[134°] Formed, together with methyl oxindole, by reducing di biomo methyl oxindole with sodium amalgam Lustrous white plates, v sl. sol cold water, v sol hot alcohol Not decomposed by boiling aqueous KOH

D₁-bromo methyl oxindole $C_0H_4 < \frac{CBr_2}{NMe} > CO$. [204°] Formed by the action of NaOBr on methyl indole carboxylic acid (Fischer, B 17, Yellowish white tables, v sol alcohol, insol cold water Melts at 204° when quickly heated, but 180° when slowly heated Converted by boiling water into methyl w isatin Phenylhydrazine gives the phenyl hydrazide of methyl-

D1 - methyl - oxindole C, H, NO $\begin{bmatrix} 5 & 3 & 1 \\ 2 & 1 \end{bmatrix}$ $C_0H_2(CH_3)_2 < CH_2 > CO$ Carbomesyl An hydride of amido di methyl phenyl acetic acid [282°] Prepared by reduction of (2 5 3 1) nitro di-methyl-phenyl acetic acid with tin and HCl (Wispeh, B 16, 1580) Sublimable White needles Sol hot alcohol and hot benzene sl sol hot water and cold alcohol and ether, insol cold water

 $C_eH_e < CH(OH) > CO$ Methyl di-oxindole NMe Di-oxy methyl indole [151°] Formed by re ducing methyl v isatin with sodium amalgam or with zinc and HCl (Colman, C J 55, 8, A 248, 121) Needles or prisms (from benzene), m sol water, alcohol, and benzene Oxidising agents

reconvert it into methyl-\psi isatin METHYL-OXY-BENZOYL-GLYCOCOLL

ANISURIC ACID

OXYBUTENYL KETONE DI-METHYL CARBOXYLIC ACID ANHYDRIDE C,H,O, 1 c $CH_{2} CO CH < CO O > CMe$ Isocarbopyrotri Obtained from its ether by boiling with 20 p c aqueous NaOH, and ppg with dilute H₂SO₄ (Knorr, B 22, 163) Possesses great re ducing power Decomposes at 200°-209°, leaving an oil C, H,O,, which solidifies on cooling This is composed of two bodies, one being an acid v sl sol most solvents and melting at 175°, the other crystallising from ether in long prisms [60°], and giving an acid solution in water forms acetonyl acetone

Ethyl ether EtA' [110] (c 280° at 15 mm) Obtained by heating di acetyl succinic ether at 170°-180°, pyrotritaric and carbo pyrotritaric ethers being also formed (Knoir, B 22, 159) Slender needles (from hot water), v sl sol water and dilute acids, v sol alkalis, ether, chloroform, and hot alcohol Possesses great reducing power FeCl₃ gives a fine blue colour to its solution With phenyl-hydrazine it yields di oxy-di phenyl di methyl dipyrazyl N NPh CO CO NPh N

Hydroxylamine ap Č(CH₃) ĆH—ĆH— —ĊMe pears to form the corresponding di oxy di methyl-NOCOCOO N

dioxazyl | CMe CH CH_ _ĈMe

DI - METHYL - DI - OXY - BUTYLENE DI -**KETONE** CH₂ CO CMe(OH) CMe(OH) CO OH₃ [96°] Formed by reducing di methyl diketone with zinc dust and dilute H2SO4 (Von Pechmann, B 21, 1411) Needles (from ligroin) Reduces Fehling's solution in the cold FeCl, re converts it into Me CO CO Me

METHYL OXY-BUTYL KETONE C.H12O2 & 6 CH₂ CO CH₂ CH₂ CH₂ CH₂OH Acetyl - butyl alcohol (227°) SG 4 997, 15 989, 25 982 MM 6 502 at 18 5° Obtained by boiling the anhydride of its carboxylic acid with water, CO2 being evolved (Perkin, jun, C J 51, 717) Thick oil with sweet burning taste Does not reduce Fehling's solution or ammoniacal AgNO in the cold, but reduces both these reagents Yields an oily phenyl hydrazide on warming Warm conc HNO, gives a dark pink colour

Iodine and KOH give iodoform Chromic acid mixture oxidises it to acetic and succinic acids

METHYL OXY BUTYL KETONE ANHY-DRIDE C₆H₁₀O is O CH₂ CH CH CH CH₂ Methylfuridane dihydride 'Acetyl tetramethylene' 'Tetramethylene methyl ketone' Anhydride of aceto butyl alcohol (109°) SG 15 9127, 25 9050 MM 6 074 at 22 5° aceto butyl alcohol 4 9227, Formed by distilling its carboxylic acid at 150° (Perkin, jun, C J 51, 723, B 19, 2558) Colour less mobile liquid with ethereal &dour On prolonged standing in presence of water it is converted into

methyl oxy butyl ketone Methyl oxy butyl ketone anhydride carboxy

he acid C, H₁₀O₃ i.e O < CH₂ CH₂ CH₂ CH₂ | [119] Obtained by saponifying its ether with alcoholic potash (Perkin, jun, C J 51, 715) Colourless needles, v sol hot benzene, alcohol, chloroform, and light petroleum, v e sol water Decomposes above 119° into CO and the preceding When heated with aqueous NH, at 2003 it yields CO2, methyl oxy butyl ketone, and a volatile base (probably a derivative of pyridine) Bromine vapour gives C, H, BrO2, a thick syrup

Conc HBrAq yields methyl bromo butyl kctone Salts—NH₄A' white crystalline solid, v sol water—CuA' aq light green powder, v sl sol water, decomposed at 90°-100° -AgA' white crystalline solid, v sol water, decomposed on boiling with water or exposure to light

Ethyl ether EtA' hyl ether EtA' [9] (227') VD MM 10069 at 237° SG $\frac{15}{1}$ 1069, 25 1 0626 μ_A 1 4697 μ_D 1 4772 Formed by heating a mixture of NaOEt with aceto acetic ether and trimethylene bromide (Perkin, jun, C J 51, 709) Colourless oil with a disagree able camphor like odour Does not react with phenyl hydrazine Does not contain an atom of hydrogen displaceable by sodium With PCl, it forms C₂H₁₈O₂Cl, a colourless oil (212°-215°)

Methyl oxy butyl ketone anhydride dicarboxylic acid C,H10O, te

CH, CH CH, [185°-190°] Ob C(CH, CO,H) C CO,H

tained by saponification of its ethers by boiling alcoholic potash (Perkin, jun, C J 51, 744) Colourless hexagonal plates, v sol hot water and hot alcohol, sl sol acetic ether, benzene, and ether Decomposes on fusion, giving off CO, and leaving a red liquid

Mono ethyl ether, CH₂ CH₂ CH₂

[114°] Obtained C(CH₂ CO₂H) C CO₂Et by treating the di ethyl ether with conc alcoholic

potash in the cold Transparent four sided tri climic needles, abc = 7741337, $\alpha = 89^{\circ}40'$, $\beta = 98^{\circ}18'$, $\gamma = 89^{\circ}50'$ V sol alcohol and ether, sl sol hot water — AgEtA" white curdy pp, sl sol water

Di ethyl ether Et₂A". (239° at 150 mm) Obtained by the action of NaOEt on a mixture of trimethylene bromide and acetone di-carb-oxylic ether CO₂Et CH₂ CO CH₂ CO₂Et (Perkin, jun, C J 51, 789) Thick, colourless oil, with disagreeable odour

METHYL-OXY-CONIINE & CONINE.

METHYL-OXY-ETHYL-AMIDO-PHENOL

Methyl ether C₁₀H₁,NO₂ te
[2 1]C₂H₄(OMe) NMe CH CH₂OH Methyl-oxy
ethyl answilme (290°) Formed by the action
of C₄H₄(OMe) NHMe on ethylene chlorhydrin
(Knorr, B 22, 2098) Liquid

Anhydride C_oH, O—CH, Methyl

quinazoxine dihydride (261°) Formed by boiling the methyl ether with caustic soda (knorr, B 22, 2093) Liquid, with irritating smell, volatile with steam, very easily oxidised by contact with an B'HCl [162°] Short four cornered plates (from alcohol)

METHYL OXY ETHYL AMINÉ C.H., NO 1 e CH., NH CH. CH.2OH (130°-140°) Formed from ethylene chlorhydrin (1 mol) and methyl amine (1 mol) (knori, B 22, 2088) Oil, with strong ammoniacal smell, v sol water, alcohol, and ether Aurochloride [110°-120°] An

hydrous prisms, v sol water

Methyl di oxy di ethyl amine C,H,,NO ie CH, NOH CHOH) (270°-255°) Formed by heating ethylene chlorhydiin with excess of aqueous methylamine at 100° (Morley, B 13, 222) Formed also by the action of ethylene chlorhydrin on the pieceding body (Knorr, B 22, 2081) Viscad oil, v sol water, not volatile with steam —B'HOI thick syrup —B',H PtOI, orange red piisms—Autochloride v sol water

Methylo chloride C₃H₁₆NO Cl ie ClNMe (CH₂CH₂OH)₂ Formed by heating ethylene chlorhydrin with a solution of dimethyl amine at 100 (Morley B 13, 223) Formed also from dimethyl oxy ethyl amine and ethyl ene chlorhydrin (Knorr B 22, 2089) Thick syrup – (CH₂NO Cl) PtCl, aq [218³] Small yellow crystals, v sol water, sl sol alcohol — Aurochloride [233³], small plates, v sol hot water

Anhydride CH, NCH CH2>0 Methyl

pmoxame tetrahydride (117) Formed by heating methyl di oxy di ethyl amine with SO₃ (h) Mixes with water, alcohol and ether Readily combines with MeI—Hydrochloride [205°], long hygroscopic prisms—Platino chloride needles (from dilute alcohol), v sol witer—Aurochloride [183°], small needles m sol water

Methylo rodide of the anhydride Long needles With Ag O it yields a methylo hydroxide, which is split up by heat into alde hyde and di methyl oxy ethyl amine

Methylo chloride of the anhydride Crystalline mass Forms a platinochloride crys tallising from alcohol in needles, and an amo

chloride, both being v sol water

Di methyl oxy ethyl amine C₄H₁₁NO is NMe, CH, CH, OH Di methyl ethyl alkine (1 10°) Prepared from dimethylamine and ethylene chlorhydrin (Ladenburg, B 14, 2408) Formed also by heating 'methyl morphi methine' (v Morphine) with Ac₂O at 160°-190° (Knorr, B 22, 1114) Liquid—B'₂HAuCl₄ needles, sol hot water—B'₂H₂PtCl₈ easily soluble prisms

Acetyl derivative C,H1,AcNO Forms an aurochloride B'HAuCl,, crystallising in plates Vol. III

Methylo hydroxide v Neurine TRI-METHYL-OXYETHYL-AMMONIUM HYDROXIDE v Neurine

METHYL OXYETHYL ANILINE

C₂H₁₃NO ie C₂H₃N(CH₃)(C₂H₄OH) Methyl phenyl ethyl alkine (218° at 110 mm) S G ² 10806 Obtained by heating methyl anline with ethylene chlorhydrin at 100° (Laun, B 17, 675) Colourless oil Weak base By exposura to air it is oxidised to a thick blue syrup

Methylo nodide B'MeI colourless plates

or *ables

Methylo-periodide B'MeI, [87°]

greenish clistening plates

METHYL a OXY ETHYL RETONE C.H.O.

1e CH. CO CH(OH) CH. (142°) ketoxy butane

Formed by reducing di methyl diketone with

zinc and H.26O. (Yon Pechmann, B 22, 2214,
23, 2421) Colourless liquid, miscible with

water Reduces Fehling's solution Reacts

with phenyl hydrazine, with formation of the

compounds CH. C(N HPh) CH(OH) CH. [84°]

and CH. C(N HPh) C(N.HPh) CH.

METHYL OXY ETHYL PYRIDINE t TROP

METHYL OXY ETHYL p TOLUIDINE

C₁₀H₁₅NO : e CH OH CH₂ NMe C₂H₄Me (290°–300°) Formed from oxy ethyl toluidine and MeI at 60° (Demole, A 173, 129) Liquid — B'HI —B H PtCl₂

Methylo rodide B Mel Liquid Yields

B'2Me.PtCl, and B MeAuCl,

METHYL OXY GLUTARIC ACID $oldsymbol{v}$ Oxy methyl clutaric acid

TRI METHYL TRI OXY HYDROBENZ AMIDE & ANISHYDRAMIDE

TETRA METHYL OXY TRIMETHYLENE-DIAMINE C H₁₈N₂O vc HO CH(CH. NMe₂), Tetra m thyl oxy propulenc diamine Tetramethyl allyl alkine (170°-185) Formed by heating s dichlorhydrix. CH Cl CH(OH) CH, Cl with dimethylamine in a sealed tube at 60° (Berend, B 17, 510) The liquid is rendered alkaline by kOH and extracted with chloroform L quid, v e sol water—B'.H₂PtCl₆ yellow plates, m sol water

DI METHYL TRI OXY PHENYL BENZYL-KETONE t ANISOIN

DI METHYL OXY PROPYL AMINE

C,H₁₃NO (126°) Prepared by the action of dimethylamine on propylene chlorhydrin at 100° (Morley, *C R* °1, 333, Ladenburg, *B* 14, 2407) Liquid—B₂H PtCl_s pri-ms v sol water

Methylo chloride B McCl Prepared by heating aqueous timethylamine with propylene chlorh drin at 100° (Morley, C R 91, 333, B 13, 1805) Colourless, very hygioscopic crystals, turning brown in light Forms a platinochlorida B',Me PtCl, crystallising in yellow feathery plates, insol alcohol and ether, v sol water

Methylo hydroxide B'MeOH From the chloride and moist Ag O Alkaline syrup Decomposed on distillation into NMe, and propylene

glycol (Morley, C J 41, 389)

D1-methyl dioxypropyl amine C₅H₁₈NO₂ to NMe₂CH₂CH(OH) CH₂(OH) D1 methyl propylglycolline (217) Formed by heating dimethyl amine with glycerin chlorhydrin (Roth, B 15, 1153) Colourless oil Sol water, alcohol, and other —B'₂H₂Cl₂PtCl₂

AA

C_eH_{1e}NO₂Cl 2 e H) From glycerin Methylo chloride Methylo chioride CallenO201 12

MecCl.CH.,CH(OH) CH_4(OH) From glycerin chlorhydrin and NMe, at 100° (V. Meyer, B 2, 186, Hanriot, A Ch [5] 17, 99) Crystals, v e sol water — (C.H.,NO.COL),PtCl, tables — C.H.,NO.CAUCI, [190°] Orange crystals

METHYL OXYPROPYL-ANILINE C.,H.,NO.

* & C,H, N(CH,)C,H, OH Methyl phenyl propyl-alkine (262°) Colourless liquid Formed by heating methyl aniline with propylene chlor

hydrin (Laun, B 17, 678)

METHYL & OXYPROPYL KETONE C.H. O.

 te
 OH, CO CH, CH, CH, CH, OH
 Acetyl propyl

 alcohol
 (145°) at 100 mm , (209°) at 729 mm

 V D 2 25 (calc 8 53)
 S G 15 10051, 25 9990

 M M 5 544 at 25°
 Formed by boiling trimethyl
 ene methyl ketone carboxylic acid (derived from aceto acetic ether, sodium, and ethylene bromide) with water, CO2 being evolved (Perkin, jun, C J 51, 829) Formed also by boiling bromo ethyl aceto acetic ether with aqueous HCl Thick syrup, miscible with water, v sol alcohol and ether Decomposed by heat into water and its anhydride, which reunite in the cold, does not reduce cold ammoniacal silver nitrate, but reduces it on warming Gives with phenyl hydrazine solution an oily precipitate of $C_{11}H_{14}N_2$ or CH_2 CMe N CH_3 Oxidised by $K_1Cr_2O_2$ and H_2SO_4 to acetyl propionic (levulic) acid (Colman a Perkin, C J 53, 189, 55, 352, Lipp, B 22, 1196) Reduced by sodium amalgam to CH₃ CH(OH) CH₂ CH₂ CH₂OH (Perkin, jun, a Freer, B 19, 2566) With NaHSO₃ it forms CH₃.C(C₃H₆OH)(OH) SO₃Na 1 ¹/₂aq needles, v sol water and alcohol

Acetyl derivative CH, CO C, H, OAc (214° 1 V) at 728 mm SG \(\frac{5}{6} \) 1 0356 VD 502 (calc 498) Liquid, m sol water, v e sol alcohol and ether

Benzoyl derivative CH3 CO C3H6OBz

Anhydride CH₃ C CH CH₂ C CH. $(72^{\circ}-75^{\circ})$

Formed by slow distillation of the ketone Water converts it into the flocculent isomeride

CH₂ CH₂ CH₂ C< (111°) at 718 mm, which CH,

reddens pine wood moistened by HCl v Methyl ENE FURFURANE TRIHYDRIDE

Methyl ω -oxy-propyl ketone $C_3H_{10}O_2$ ieCH, CO CH(OH) CH₂ CH₃ (153°), (77° at 35 mm) $S G \frac{17.5}{4} 972$ Formed by reducing methyl ethyl diketone with zinc and dilute H₂SO₄ (Von Pechmann, B 23, 2421) Colour less liquid with sweet smell, sol water, but separated from the solution by NaCl or NaOH Readily oxidised to CH, CO CO C.H. Reduced by sodium amalgam to CH, CH(OH) CH(OH) C2H, (187°), which is oxidised by bromine water in sunlight to CH, CO CO C₂H₅ Excess of phenyl sunlight to CH₃ CO CO C₂H₃ Excess of pheny hydrazine forms CH₃ C(N₂HPh) CO C₂H₃ [103°]

Methyl a-oxy-propyl ketone $C_3H_{10}O_2$ to CH_3 CO CH_2 CH(OH) CH_4 (128°) Formed by adding chloro acetic ether to sodium under ether, decomposing the resulting sodium compound by HCl, reducing by zinc dust the ether C₂H₁₂ClO₄ (157° at 45 mm) which is then

formed, and boiling the product C.H., O. (106° at 14 mm), with dilute HCl, when it splits up into CO₂, alcohol, and the oxy ketone (Fittig, B 21, 2138) Colourless mobile liquid, miscible with Forms compounds with NaHSO, and water with phenyl hydrazine

Methyl w oxy isopropyl ketone Oxim of (CH₃)₂C(ONO₂) C(NOH) CH₃ thenitrateFormed by the action Pentane nitroso nitrate of amyl nitrite and nitric acid on amylene (CH_s), C CH CH_s (38°) dissolved in HOAc (Wallach, A 248, 162) Monoclinic crystals, a b c = 97711449, $\beta = 83^{\circ} 32'$ (from benzene), or needles (from HOAc)

METHYL OXY QUINIZINE v OXY PHENYL-METHYL-PYRAZOLE

METHYL OXY QUINOLINE v OXY METHYL-QUINOLINE

METHYL OXY SUCCINIC ACID v METHYL SUCCINIC ACID

METHYL PARABANIC ACID v PARABANIO

METHYL PARACONIC ACID v Anhydride of OXY FTHYL SUCCINIC ACID

TETRA METHYL-PARALEUCANILINE Tetra methyl tri amido tri phenyl methane

METHYL PENTADECYL RETONE C17H14O ie CH₃ CO C₁₅H₃₁ [48°] (246°) at 110 mm, (320° uncor) at 760 mm S G (liquid) 48 814 Prepared by distilling a mixture of barium palmitate and barium acetate (Krafft, B 12, 1671) On oxidation it gives pentadecoic acid

Methyl pentadecyl ketone CH, CO CH(C,H₁). Di n heptyl acetone (300°-304°) SG 17 826 Formed by boiling di heptyl acetoacetic ether with dilute aqueous KOH (Jourdain, A 200, 115) Oil, smelling of Forms a crystalline compound peppermint with NaHSO,

METHYL PENTANE v HEXANE

DI-METHYL PENTENYLAMINE C, H, N & e CH₂ CH CH₂ CH CH₅ NMe This constitution is assigned by Merling to Ladenburg's di methyl piperidine, v Di mfthyl pyridine hfxa

Di methyl pentenylamine Methylodroxide C, H, NMe, OH Formed from amylene bromide and trimethylamine at 55° (Schmiedeberg a Harnack, J 1867, 805 (C₃H₉NMe₃Cl)₂PtCl₄ aq Irregular lamınæ 805)

(β) METHYL PENTHIOPHENE C₆H₈S ι ε s<CH CMe>CH. (134°) SG 18 9938 Formed by distilling sodium a methyl glutarate CO₂Na CHMe CH CH₂ CO Na (5 g) with P₂S₄ (10 g) at 180°-250° (Krekeler, B 19, 3270) Colourless oil When successively mixed with a solution of isatin in HOAc and cone H2SO, it gives a dark green colour, and, on adding water, Phenanthraquinone and H2SO4 a green pp (Laubenheimer's reagent) give a dark violet colour Phenyl glyoxylic acid yields a violet dye Alkalıne KMnO, (3 p c) produces acetto and oxalıc acıd Nıtrıc acıd forms a nıtroderivative, and bromine a biomo- derivative

Methyl penthienyl methyl ketone CaH, SO 1.e SC₅H₄Me CO CH₃ (284°)

Oxim SC, H, Me C(NOH) CH, [689]. METHYL - PHENACYL - ANILIDE

a Phenyl-amido phenyl ethyl ketone.

(above

METHYL - PHENACYL - BROMIDE

Bromo phenyl ethyl ketone

METHYL-PHENANTHRIDENE & PHENYL-

METHYL-PHENANTHROLINE C₁₂H₁₀N₂ 2 e CH N C CH CH C CH CH

CH CH C C N CMe (65°)

CH CH C—— C N CMe 360°) Formed, together with an isomeride, when m amido $(Py\ 3)$ methyl quinoline $(100\ g)$ is boiled with o nitro phenol $(75\ g)$, glycerin $(320\ g)$, and H_3SO_4 $(270\ g)$ The product is diluted with water and evaporated to remove o nitrophenol The resinous mass that is ppd on adding NaOH is extracted with benzene, and the dark oily mixture of bases so obtained with alcohol, dissolved in water, decomposed by NH,, and the bases again extracted with benzene From the crystalline mixture of bases left after evaporating the benzene, ether extracts methylphenanthroline only (Gerdeissen, B 22, 246)

Properties — White needles (containing 3 aq) Melts at 50 when hydrated, 65° when anhydrous Sol boiling water, alcohol, and ether, v sol cold benzene On oxidation with KMnO, it yields phenanthroline carboxylic acid C₁₂H,N,CO H [209°], which decomposes at 210° into CO, and

phenanthroline

Salts B'HClaq small snow white needles, al sol cold, v sol hot, water, m sol alcohol, nsol ether - B'H SO, aq slender silky needles (from alcohol) --B',H,Gr,O, red prisms (from hot water) - B'H,PtCl₆ aq flesh coloured crystalline pp, insol, hot water, sl sol alcohol -- Picrate BC,H,(NO),3OH [217°] Transparent yellow needles (from boiling alcohol) Ethylo rodide B'Etl 2aq [100°-110°]

Ethylo rodide BEII 2aq [100°-110°] Glittering brown crystals Lields the platino chloride BEtClH,PtCl₄(?) which forms orange

red crystals

Isomeride C₁₃H₁₀N₂₁ & CH N C CH C N C Ne

cold ether, v sl sol hot ether

Methyl phenanthroline
CH N C C N C N e

[76°] Prepared
[76°] Prepared

CH CH C CH CH CH CH CH CH from o amido (Py 3) methyl quinoline, glycerin, o nitro phenol, and H₂SO₄ (Gerdeissen) Crystals (containing 2aq) Meltat 53° when hydrated, and at 76° when anhydrous V e sol hot benzene, v sol chloroform, m sol HOAc, sl sol ether and light petroleum Decomposed on distillation

Methyl-phenanthroline CH N C CMe CH C CH CH

CH CH C CN CH

O N CH

Slove

O N CH

Slove

O N CH

Slove

fied by means of the chromate (Skraup a Fischer, M 5, 523) Short prisms (containing 5aq), more soluble in cold than in hot water, v sol alcohol. Its solutions give a white crystalline pp with AgNO, and a blue crystalline pp with cupric acctate Chromic acid mixture oxidises it to the corresponding phenanthroline carboxylic acid

Salts—B'HCl 4aq transparent needles—B'₂H₂Cr₂O₇ red, sparingly soluble needles—B'₂H₂PtCl₂ 2aq yellow crystalline pp—Picrate

DI-METHYL-PHENANTHROLINE TETRA-HYDRIDE

Formed by the action of acetic aldehyde or paraldehyde upon m phenylene diamine hydro chloride. The resulting base is ppd by am monia, dissolved in aqueous HCl, and ppd by platinic chloride as B',H,PtCl_a (Schiff, A 253, 323).

METHYL PHENAZINE C13H10N2 26

 $C_{\bullet}H$ $C_{\bullet}H_{3}Me$ [117°] (350°) Formed

by heating tolylene o diamine with pyrocatechin in sealed tubes at 210° (Merz, B 19, 725) Formed also by eliminating the two NH2 groups by means of the diazo reaction, from the oxidation product $(C_{12}H_{14}N_4)$ of phenylene p diamine and tolylene m diamine (Bernthsen a Schweitzer, B 19, 2604, A 236, 345) Needles (by sublimation) v sl sol water and ligroin, v sol. alcohol and ether Its solution in conc H₂SO₄ is blood red It disolves in conc HClAq, but the base is ppd again on dilution - Salts -B' H PtCl, 6aq yellow laminæ (from water) -B'H,PtCl, 3aq (from dılute alcohol) B'C,H (NO),OH [168°] Picrate Yellow nodules which blacken on fusion

METHYL PHENTRIAZINE C,H,N, s.e

C.H. | [89°] (250° 255°) Formed

by the action of sodium amalgam on acetyl o nitro phenyl bydrazine in alcohol, the solution being kept acid with HOAc, and the tempera ture below 30° (Bischler, B 22, 2806) Crystals, partially decomposed on distillation V sol cold water, v e sol alcohol, sl sol hot ligroin

Bromo methyl phentriazine C_eH_eBrN₃ 26 CBr CH C N CMe

| | | | | | [115°] Formed from CH CH CN N acetyl p bromo o nitro phenyl hydrazine by like treatment (Bischler a Brodsky, B 22, 2818) Golden plates, sl sol cold, v sol hot, water

(a) METHYL - PHENTETRAZINE DIHY-NH N DRIDE C,H,N, te C,H, | | [62°]

Formed by the action of sodium intrate on a very dilute hydrochloric acid solution of o amidophenyl methyl hydrazine (Hempel, J. pr. [2] 41, 176) Colouriess plates, v sol ether and benzene, sl sol alcohol and petroleum ether Sol hot cone NaOHAq Cone HNO, at 80°-100° yields a product [127°] crystallising from alcohol in golden yellow prisms and needles

A & 3

TRI-METHYL PHENENYL TRIKETONE C₁₂H₁₂O₂ te C₂H₃(CO CH₄), [163°] Tracetyl-bensene Formed by the action of NaOEt in ether on a mixture of acetone (1 mol) and allyl formate (1 mol) Sodium aceto acetic aldehyde slowly separates, and is then dissolved in ice cold water and neutralised by HOAc The free aceto acetic aldehyde changes to tri acetyl benzene and water (Classen a Stylos, B 21, 1145) Small needles, sl sol water, alcohol, and ether, v sol HOAc Oxidised by HNO, to trunesic acid

METHYL - (αβ) - PHEN - NAPHTHAZIÑE CH CH C N C CH CMe C,,H,2N2

- CNCCHCH [142°] Formed by the action of (3)-naphtho quinone on tolylene diamine in HOAc (Hinsberg, A 237, 342)

Methyl-(ββ) phen-naphthazine C₆H₄ CH C N C CH CMe CH C N C CH CH [180°] [180°] Formed by oxidation of a mixture of (3) naphthol and tolylene o-diamine with alkaline K, FeCy, (Witt, C N 49, 404) Pale straw coloured needles, forming an intense red solution in H SO,

METHYL PHENOL v CRLSOL

Di-methyl-phenol v XYLENOL Tri-methyl-phenol C₆H₂Me, OH [1 2 3 5] Hemmellithenol Hemellithenol [81°] Formed by fusing hemimellithene sulphonic acid with KOH (O Jacobson, B 19, 2518) Needles (from Gives no pp with FeCl,

Tetra methyl phenol C₆HMe₄ OH [1 2 3 4 5] [81°] (L), [87°] (T), (249° uncor) (L), (266° 1V) (T) Formed by the action of nitrous acid on the corresponding C₆HMe, NH [66²] (Limpach, B 21, 644), or by fusing c tetra methyl-benzene sulphonic acid with potash (Tohl, B 21, 907) Long white needles (from very dilute alcohol), v e sol alcohol and ether, m sol petroleum ether Volatile with steam Bromine foims C₁₀H, Br OH [151°]

Acetyl derivative C10H13OAc [57°] Prisms

Tetra-methyl-phenol C,H(CH,), OH Formed by the action of nitrous acid on tetra methyl-phenyl amine $[14^{\circ}]$ (Hofmann, B 17, 1916) White crystals Yields a quinone on White crystals distillation with MnO2 and H2SO4

Ethylether C.H(CH,)4OEt (236°), liquid Formed by the action of alcohol upon the sulphate of tetra methyl-diazo benzene (Hofmann, B 17, 197)

Penta-methyl-phenol C₆(CH₂), OH [125°] (267°) Formed by the action of nitrous acid upon penta methyl-phenyl amine (Hofmann, B 18, 1826) Fine white needles Volatile with steam Soluble in alcohol Sparingly soluble ın alkalıs

Methyl ether C₆(CH₃), OCH₃ [64°], long needles

METHYL-DIPHENYL C13H12 1 e C.H. C.H.Me [3 1] Phenyl-tolyl (275°) SG 2 1031 Formed by the action of McGl upon melted diphenyl in presence of Al,Cl, (Adam, Bl [2] 47, 689, 49, 98, A Ch [6] 15, 239) Lumpid colourless liquid, not solidified at -21° V e sol methyl alcohol and acetone attacked by KMnO, either in neutral or alkaline solution. Chromic acid oxidises it to diphenyl

m carboxylic acid [161°] Bromine at 150° forms C₁₂H₉ CH₂Br which when treated with KOEt yields C12H, CH2OEt whence dry gaseous HI liberates phenyl benzyl alcohol

o Methyl-diphenyl C13H12 1 e CaH, CaH, Me[2 1] (259°) Appears to be formed by treating bromo benzene mixed with liquid bromo toluene with sodium (Barbier, B 7, 1548)

p Methyl-diphenyl CeH, CeH, Me[4 1] (263°-

267°) SG 27 1 015 Formed by the action of sodium on an ethereal solution of bromo benzene and p bromo toluene (Carnelley, C J 29, 13) Formed also by passing a mixture of benzene and toluene through a red hot tube (Carnelley, C J 37, 701) Solidifies at -2° Dilute nitric acid oxidises it to diphenyl carboxylic acid. Chromic acid forms terephthalic acid

Di-methyl-diphenyl $C_{14}H_{14}$ i ι $C_{15}H_{5}Me_{2}$ $4^{\circ}-290^{\circ})$ S G $\stackrel{\circ}{=}$ 1 025 Formed by the (284°-290°) action of methyl chloride on diphenyl in presence Colourless liquid, not solidi of Al₂Cl₆ (Adam) Oxidised by CrO₃ in HOAc fied at -21° yielding an infusible diphenyl dicarboxylic acid which cannot be sublimed

Other di methyl-diphenyls are described as DITOLYLS

DI - METHYL-PHENYLACETAMIDINE C10H14N 1 e C2H2 CH C(NHMe)(NMe) Formed by the action of alcoholic methylamine on the hydrochloride of phenylacetic imido ether C₀H₅ CH C(OEt)(NH) (Luckenbach, B 17, 1426) Crystalline solid, v sol alcohol —B'HCl six sided prisms — B' H PtCl, small glistening crystals, sol alcohol, sl sol water

u Di methyl-phenylacetamidine C₆H₃CH₂C(NMe₂)(NH) Formed in the same manner as the preceding, using dimethylamine (L) -B',H.PtCl, small needles, sl sol water, m sol alcohol

DI-METHYL-PHENYL-ACETIC ACID

[5 3 1]C₈H₃(CH₃)₂ CH₂ CO H Mesityl-accite acid [100°] (W), [97°] (Robinet, Bl [2] 40, 316) (273° at 735 mm) Formed by the saponifica tion of the nitrile obtained by heating mesityl bromide with KCN (Wispek, B 16, 1578) Long white prisms Sol alcohol, ether, and hot water, v sl sol cold water

Salts -A'K aq silky needles - A' Ba 4aq transparent prisms -A', Ca 3aq easily soluble thick needles -A'2Mg 5aq long silky needles -A'Ag long thin needles

Tetra-methyl-phenyl-acetic acid $C_{12}H_{16}O_2$ i e IMe, CH_2 CO_2H [5 4 3 2 1] [125° uncor] C₆HMe₄ CH₂ CO₂H [5 4 3 2 1] Formed by reducing the corresponding tetra methyl mandelic acid with HI (Claus a Fohlisch, J pr [2] 38, 234) Slender needles (from hot water), v sol alcohol, ether, and chloroform -CaA', 3aq silky needles

TRI-METHYL-PHENYL-AMIDO-CROTONIC ACID v \(\psi \) CUMYL AMIDO CROTONIC ACID

Tetra-methyl phenyl-amido-crotonic Ethyl ether CoHMe, NH CMe CH CO2Et [101°] Obtained by the action of tetra methyl phenyl amine (prepared from ψ -cumidine) on acetoacetic ether (Conrad a Limpach, B 21, 1655) Large white prisms (from alcohol and ether) At 280°-285° it yields oxy tetra-methyl phenyl-di-methyl-pyridine carboxylic $C_{\bullet}HMe_{\bullet}N < CMe_{OMe_{OH}} C(CO_{2}H) > CO.$ [145°]

METHYL-PHENYL AMINE vTOLUIDINE and METHYL-ANILINE

Di-methyl-phenyl-amine v Xylidine and DI METHYL ANILINE

Tri methyl-phenyl amine v MESIDINE and **♦** CUMIDINE

Tetra methyl phenyl amine

(260° uncor) $C_6HMe_4(NH_2)[1\ 2\ 3\ 4\ 5]$ [66°] Obtained by heating isocumidine hydrochloride with McOH at 250° to 260° under pressure (Limpach, B 21, 644) Nacieous leaflets (from The corresponding water) May be sublimed C.HMe.(OH) melts at 81°

Formyl derivative [144°], silky needles

(from water)

Acetyl dernature [170°], silky needles Tetra methyl phenyl-amine C₆HMe₄NH., [1 2 3 5 6] Isoduridine [24°] (255°) Formed by heating the hydrochlorides of ψ cumidine or mesidine with MeOH at 300° (Hofmann, B 17, 1912, Nolting a Baumann, B 18, 1149, Limpach, b 21, 646) -B'HCl -B' H. PtCl,

needles

Acetyl derivative C. HMe, NHAc [215°] Tetra methyl-phenyl amine C.HMe, NH2 Duruline [14°] (253°) SG $\frac{21}{2}$ 978 product of the action of McOH on xylidine hydrochloride at a high temperature (Hofmann, B 17, 1913) -B'HCl B' H PtCl

Penta methyl phenyl amine C₆(CH₃) NH₂ 1mido penta methyl ben enc (152 (278°) Prepared by heating dimethyl ψ cumidine with methyl iodide under pressine at 240°-200° (Hof mann, L 18, 1821) Large colourless needles V sol alcohol and ether, msol water On oxi dation by arsenic acid in conjunction with aniline, it yields a homologue of rosaniline MeI at 100° forms (Mc NHVe 61 , which is not further acted on by MeI even at 170

Salts -b'HCl long thin needles, easily soluble in hot water, sl sol cold -b H Cl PtCl, sparingly soluble trimetine tables - The acetate is very soluble the nitrate forms sparingly soluble needles, the sulphate and oxalate very sparingly soluble small scales

Acetyl dernatue C_s(CH₃) NHAc

[213°], needles

METHYL DI PHENYL AMINE C13H13N 1 e. NPh Me Di phenyl methyl amina (282°) (G) (292°) at 741 mm (Bruhl, A 235, 21) S G 24 1 0476 Formed by methylation of diphenyl amine (Bardy, Z 1871, 649, Giraid, Bl [2] 23, 2) Liquid Gives a violet colour with HNO, Fuming HClAq at 150 resolves it into McCl and diphenylamine (Gnehm B 8, 1040) By passing through a red hot tube it is converted into diphenylamine, carbazole, benzonitiile, aniline, benzene, methane, hydrogen, nitrogen, and other products (Graebe, A 174, 181) Nitrous acid passed into its alcoholic solution yields NMePh C₈H₄ N_rC₈H₄ NMePh Boiling nitric acid forms a compound which crystallises from alcohol in yellow prisms [284°]

Derivatues -Tri bromo and BROMO-DI NITRO , METHYL-DIPHENYLAMINE

METHYL - PHENYL - ANTHRACENE PHENYL-METHYL-ANTHRACENE

METHYL-PHENYL-CARBAMIC ACID TOLYL CARBAMIC ACID

Di methyl phenyl carbamic acid c. XYLYL-CARBAMIC ACID

Tri methyl phenyl carbamic acid Ethul ether C_bH₂Me₃ NH CO₂Et ψ Cumyl-carbamic ether [915°] Formed by the action of chloroformic ether ClCo, Et on \(\psi \) cumidine (Frentzel, C C 1888, 1361) P₂O₃ converts it into the cyanate C₅H Me₃NCO (221°), polymerised by PLt, or KOAc into the cyanurate [234°]

Tri methyl phenyl carbamic acid Ethyl ether C.H Me, NH CO, Et Messtyl-urethane [62°] Formed from messidine and ClCO, Et (Eisenberg, B 15, 1016) Long colourless needles, volatile with steam, sol alcohol and

TETRA METHYL-PHENYL CARBAMINE C,H(CH₃), NC [51°] White crystals by heating tetra methyl phenyl amine [14°] with chloroform and alcoholic KOH It is changed into the nitrile by distillation (Hofmann, B 17, 1914)

Penta-methyl phenyl carbamine

Formy l derivative [183°], long silky C6(CH3), NC [128°] Formed by heating pentamethyl phenyl amine with chloroform and alcoholic NaOH (Hofmann, B 18, 1824) Colourless crystal- V sol alcohol At a few degrees above its melting point it is transformed into the nitrile with evolution of heat

> METHYL TRI PHENYL CARBINOL CARB OXYLIC ACID & DI PHENYL TOLYL CARBINOL-CARBOXYLIC ACID

METHYL PHENYLENE DIAMINE

v PHENYLINE METHYL DIAMINE

Di methyl phenylene diamine v Phenylene DI METHYL DIAMINE

Tri methyl phenylene diamine CoH14N2 1.6 C, HMe, (NH), [1 2 4 3 5] [81°] Formed from nitio ψ cumidine by reduction (Mayer, B 20, 970) Long needles, v sol benzene FeCl₂ colours its solution deep red

Isomerides : DI AMIDO MESITYLENE and DI-AMIDO # CUMFNE

Tetra-methyl phenylene diamine C, H, N, 1 c *C, Me, (NH,) [1 2 4 5 3 6] Formed by reducing di nitio s duiene with zinc and HOAc (Nef, 4 237, 4) Pearly plates, v sol chloroform and alcohol, m sol ether Its solutions are coloured green by atmospheric oxidation FeCl, yields duroquinone The hydrochloride 18 sl sol cone HClAq

Tetra-methyl phenylene diamine

C₆Me₄(NH₂)₂[124356] Prehnitylene-diamine [140°] Formed by reducing C₆Me₄(NH₂)(NO₂) with tin and HCl (Tohl, B 21, 906) Plates (from water), or needles (from alcohol), v e sol alcohol, sl sol ether and ligroin -B"H,Cl, aq plates, v e sol water, v sl sol. conc HClAq Coloured dark red by FeCl,

METHYL-DIPHENYLENE KETONE OXIDE v Phenylene tolylene ketone oxide

DI-METHYL PHENYLENE-DIVINYL DI-KETONE C₁₄H₁₄O₂ te C₅H₄(CH CH CO CH₄)₂.
[156°]₅ Formed by the action of NaOHAq on a mixture of acetone (10 pts) and terephthalic aldehyde (1 pt) (Loew, A 231, 379) Needles, almost insol water, alcohol, and ether, v sol. chloroform, v e sol acetone With cone H.SO. it yields a deep-red solution

METHYL - PHENYL - ETHYL - ALKINE . METHYL-OXYETHYL ANILINE

METHYL PHENYL-ETHYL KETONE v BENZYL-ACETONE

METHYL PHENYL-GLYOXYLIC ACID of TOLYL-GLYOXYLIC ACID

Di-methyl-phenyl glyoxylic acid v XYLYL-GLYOXYLIC ACID

Tetra-methyl phenyl glyoxylic acid [65321] C.HMe, CO CO.H [124°] Formed by oxidising the ketone C.HMe, CO CH, with cold aqueous KMnO, (Claus a Foecking, B 20, 8102) White scales, sl sol water, v sol alcohol and ether Reduced by sodium amalgam to tetramethyl-mandelic acid C₆HMe₄ CH(OH) CO₂H -KA' 5aq crystalline, v e sol water — CaA', 9aq nodules —BaA', 3aq nodules —AgA' white pp

Tetra-methyl phenyl glyoxylic acid [64321] C.HMe, CO CO.H Formed by oxidising the corresponding duryl methyl ketone with cold aqueous KMnO. (C a F) Yellow with cold aqueous KMnO, (C a F) Yellow liquid, al sol water, v sol alcohol and ether Solidifies when strongly cooled amalgam reduces it in alcoholic solution to the corresponding tetra methyl mandelic acid -NaA' 5aq white crystalline crusts —BaA', 5aq nodules —CaA', 23aq granules —CuA', 25aq green crystals, v sol water —PbA', white pp, v sl sol water -AgA' white pp , insol water

Tetra-methyl-phenyl-glyoxylic acid C12H14O3 se [54321] C.HMe, CO CO2H Formed by oxidising the corresponding tetra methyl phenyl methyl ketone (Claus, J pr [2] 38, 232) BaA' 4aq needles — CaA' 4aq nee Oil -BaA', 4aq needles -

CuA', 3aq

Penta-methy: phenyl-glyoxylic acid C₁₃H₁₆O₂ te C₆Me, CO CO₂H [122°] Formed by the action of AlCl, on a mixture of penta methyl benzene and ClCO CO Et (Jacobsen, B 22, 1218) Formed also by oxidising CoMe, COCH, with alkaline KMnO. Prisms, v sl sol cold water, v sol alcohol —NaA'3aq plates, m sol cold water —BaA', 5aq nodules, v sl sol cold water

-CuA', 5aq needles
HEXA METHYL DI-PHENYL GUANIDINE C₁₈H₂₈N₃ te HN C(NH C₈H₂Me₈)₂ Dr mesityl guanidine [218°] Formed by heating SC(NH C.H.Me.)2 with alcoholic NH, and lead oxide (Eisenberg, B 15, 1014) Minute prisms,

sol. alcohol and ether, insol water

Ennea-methyl-tri phenyl-guanidine C_{2a}H₂₅N, s.e C₆H₂Me₈N C(NH C₆H₂Me₂), [225°] Formed by heating hexa methyl di phenyl thio urea with alcoholic mesidine and lead oxide (E) Small crystals, sol alcohol, insol water

METHYL PHENYL-HYDRAZINE v PHENYL-METHYL-HYDRAZINE

Tri methyl-phenyl-hydrazine C,H14N2 & e [1 2 4 5] C.H.Me. NH NH. \(\psi \) Cumyl hydrazıne [120°] Formed by boiling its sodium sulphonate with water (Haller, B 18, 91) Needles (from ether), insol water and alkalis, v sol alcohol and ether With aceto acetic ether it yields oxy tetra methyl phenyl pyrazole

Sodium sulphonate C.H.Me, NH NH SO, Na Formed by warming diazo- ψ -cumene chloride with Na,SO, and reducing the resulting C₄H₂Me, N, SO₅Na with zinc-dust and HOAc (Haller) White plates (containing 1 aq), sl sol cold water and alcohol, v sol hot water

METHYL-PHENYL-DI-KETONE . PHENYL-

METRYL-DI-KETOME

TRI-METHYL-PHENYL MERCAPTAN

C.H. S t e C.H. Me. SH Mesttyl sulphydrate. Thromestol. (229°) S G 1 0192 Formed by reducing mesitylene sulphochloride with zine and H₂SO₄ (Holtmeyer, Z 1867, 686) Liquid, volatile with steam , v sol alcohol, ether, and benzene $-Hg(S C_6H_2Me_8)_2$ white silky needles

HEXA-METHYL-DI-PHENYL METHANE $C_{19}H_{24}$ is $CH_2(C_6H_2Me_2)_2$ Dr-mesityl methane [c 130°] Formed by the action of H₂SO, on a mixture of CH₂(OAc), and mesitylene dissolved in HOAc (Baeyer, B 5, 1098) Monoclinic prisms (from ether)

Methyl-tri-phenyl methane v DI PHENYL TOLYL METHANE

TETRA - METHYL - PHENYL - DI - METHYL AMINE C12H18N 2e C4HMe, NMe2 Formed from tetra methyl phenyl amine [14°] by treatment with MeI and alcoholic soda (Hof Colourless liquid mann, B 17, 1914) B'2H2PtCl crystalline

Penta-methyl-phenyl-methyl-amine C, H, N re C_e(CH_s), NHMe Methyl-amido penta-methyl-benzene [61°] Colourless scales Formed by heating penta methyl phenyl amine with methyl iodide -B'2H2Cl2PtCl4 needles (Hofmann, B 18, 1824)

Penta methyl-phenyl-di methyl-amine

C_e(CH₂), NMe, Di-methyl-amido-penta-methyl-benzene [54] Colourless scales Formed by digesting penta methyl phenyl amine methyl iodide in presence of an alkali methylo-10dide could not be obtained B',H,Cl,PtCl, needles (Hofmann, B 18, 1824)

TETRA-METHYL-PHENYL-METHYL-CAR-BINOL [6 4 3 2 1] C₆HMe, CH(OH) CH, Durylmethyl carbinol (above 300°) Formed by reducing duryl methyl ketone with zinc and HCl (Claus a Foecking, B 20, 3099) Pale yellow liquid

Tetra methyl phenyl-methyl carbinol [6 5 3 2 1] C_eHMe, CH(OH) CH, [72] Formed by reducing s duryl methyl ketone (C a F) White plates

METHYL PHENYL METHYL KETONE 2

TOLYL METHYL RETONE

Di methyl phenyl methyl ketone v XYLYL METHYL KETONE

Tetra-methyl-phenyl methyl ketone C, H,O te [5 4 3 2 1] O.HMe. CO CH. c Duryl methyl ketone (260°) Formed from c durene, AcCl. and AlCl₂ (Claus, J pr [2] 38, 231) Brownish, strongly refracting, oil, insol water, sol alcohol and ether Oxidised by KMnO, to tetra methylphenyl glyoxylic and c tetra methyl benzoic acids

Phenyl-hydraside [129°] Tetra methyl-phenyl methyl ketone

[6 4 3 2 1] C.H.Mo. CO CH. (254°) Formed from u durene, AcCl, and AlCl. in CS. (Claus a. Formed Foecking, B 20, 3097) Colourless oil, v sol alcohol and ether Volatile with steam Reduced by zinc dust and alcoholic KOH to the carbinol. Oxidised by KMnO, to tetra methyl phenyl-glyoxylic acid

Phenyl-hydraside Needles, decomposing at 215°

Oxim [148°] Plates Tetra-methyl-phenyl methyl ketone [6.5.3.2.1] C.HMe. CO.CH. (251%. Formed by the action of AlCl, upon s durene mixed with AcCl in CS₂ (C a F) Plates

Crystals, decom Phenyl hydrazide

posing at 225°

Penta-methyl-phenyl methyl ketone C15H18O s.e C.Me. CO CH. [85°] (286°) Formed by the action of AlCl. on a mixture of penta-methylbenzene and AcCl dissolved in CS, Jacobsen, B 22, 1218) Pearly plates, v sol alcohol, ether, and HOAc Oxidised by KMnO, to pentamethyl phenyl glyoxylic acid

DI-METHYL-PHENYL-PHOSPHINE v

PHENYL DI METHYL PHOSPHINE

METHYL-TRI PHENYL PHOSPHONIUM IODIDE v Methylo rodide of TRI PHENYL PHOSPHINE

TRI METHYL PHENYL PHTHALIDE

phthalide Phenyl mesityl carbinol carboxylic anhydride [164°] Formed by treating an alco holic solution of [5 3 1 2] C₈H. Me, CO C₆H₄ CO H with zinc and HCl (Gresly, A 234, 237) thick needles

Tri-methyl-phenyl-phthalide C, H,6O, Cumyl phthalide [140°] Prepared as above, using the derivative of \(\psi \) cumene instead of that of mesitylene (G) Small needles

Methyl-di-phenyl-phthalide vDI PHENYL

TOLYL CARBINOL CARBOXYLIC-ANHYDRIDE METHYL - PHENYL - PSEUDO - PICOLO -

STYBIL v OXY-PHENYL DI METHYL PYRIDINE METHYL - PHENYL - PROPYL - ALKINE v

METHYL-OXYPROPYL ANILINE

HEXA-METHYL-DI-PHENYL DISULPHIDE C₁₈H₂₂S₂ r e (C₆H Me₃)₂S Mesityl disulphide [125°] Formed by atmospheric oxidation of tri methyl phenyl mercaptan in alkaline solution (Holtmeyer, Z 1867, 688) Light yellow laminæ or tables, insol water, sol alcohol, ether, and benzene

OCTA-METHYL-DI-PHENYL SULPHONE v

DI DURYL SULPHONE

Deca-methyl-di-phenyl sulphone C22H30SO2 te C.Me, SO, C.Me, [985°] Formed by the action of CISO, H on pents methyl benzene (Jacobsen, B 20, 896) Very long, slender needles (from ligrom), v sol alcohol Yields penta methyl benzene when heated with conc HClAq at 170°, and in smaller quantity when distilled

TRI-METHYL-PHENYL-THIO-CARBAMIC ETHER C12H17NSO 1.4 C.H2Me2NH CS OEt or C.H2Me2N C(SH) OEt Mesityl thio urethane [88°] Formed by heating the corresponding thiocarbimide with alcohol at 140° (Eisenberg, B 15, 1015) Siender needles, sol alcohol, ether, and warm alkalis

TRI-METHYL-PHENYL THIOCARBIMIDE C,H,Me, NCS Mesityl mustard oil Formed by heating mesidine with CS, and some alcoholic potash (Eisenberg, B 15, 1012) Long needles, sol alcohol and ether

Tetra-methyl-phenyl-thiocarbimide

C₁₁H₁₂NS is C₄HMe₄NCS [65°] Formed by boiling tetra-methyl-phenyl amine [14°] with CS₂ and a little KOH (Hofmann, B 17, 1915) Crystalline solid

Penta-methyl-phenyl thiocarbimide C, H, NS 16 C, Me, NCS Formed. [86°]

together with the corresponding thio-urea, by boiling penta methyl phenyl amine with CS. (Hofmann, B 18, 1827) Needles (from alcohol), volatile with steam

TRI METHYL PHENYL THIO UREA

C₁₀H₁₁N₂S 1 e NH₂ CS NH C₆H₂Me₃ Mesityl [222°] Formed by the action of thro urea ammonia on the corresponding thio carbimide (Eisenberg, B 15, 1013) Pearly plates, sol ether and hot alcohol, insol water

Hexa methyl di-phenyl thio urea C19H24N2S 1.8 CS(NH C₆H₁Me₂)₂. Di-mesityl thio-urea Formed by heating mesidine with CS₂ (Eisen berg, B 15, 1013) Formed also by digesting tri methyl phenyl thiocarbimide with mesidine White needles in alcoholic solution H.PO, converts it into the thiocarbimide

Isomeride v DI ψ CUMYL THIO UREA

Octo methyl di phenyl thio-urea C21H28N2S ie SC(NH C,HMe,) [278°] Formed by the action of CS on tetra methyl phenyl amine [14°] (Hofmann, B 17, 1916) Four sided plates (from alcohol), sl sol alcohol

Deca methyl di phenyl-thio urea C22H22N2S ie SC(NH C₈Me₈)₂ [252°] Formed by the action of CS₂ upon penta methyl phenyl amine (Hofmann, B 18, 1827) White needles, sol HOAc v sl sol alcohol

TRI METHYL PHENYL-UREA v 4 CUMYL

Hexa methyl-di phenyl-urea C19H21N2O 1 e OC(NHC,H Me₃)₂ Dr mesityl urea [above 300] Formed by the action of mesidine on tri methyl phenyl cyanate (Eisenberg, B 15, Minute prisms, sl sol hot alcohol, insol water

Hexa methyl dı phenyl urea

 $OC(NH C_0H_2Me_3)$.. Dr ψ cumyl urea ing to Frentzel (C C 1888, 1361) this substance melts between 260° and 270° (cf vol 11 p 296)

METHYL - PHLOROGLUCINS v GLUCI

METHYL PHOSPHATES

Methyl - phosphoric acid MeO PO(OH), Formed by slowly adding methyl alcohol to cooled POCl₃ (H Schiff, A 102, 334) -BaA"2aq laminæ, much less soluble in boiling water than in warm water - CaA" (dried at 100)

Di methyl phosphoric acid (MeO), PO OH Formed by pouring POCl, into methyl alcohol (Schiff) Acid syrup, sol alcohol and ether Its salts are more soluble than those of the pre ceding acid -BaA'. (dried at 150°) pearly plates, nearly insol alcohol -SrA', 2aq -PbA', xaq -CaA'₂ (dried at 100°) very soluble nodules

(197° cor) S V 139 5 Tri methyl phosphate Me.PO. S G 2 1 238 (Weger, A 221, 89)

(Lossen, A 254, 74)

METHYL-PHOSPHINE CH, P te CH, PH, Mol w 48 (-14°) V D 24 4 (calc 24) S (ether) 70 at 0° Formed, together with di methyl phosphine, by heating PH₄I with MeI and ZnO at 150° When water is added to the product MePH, I is decomposed, with evolution of MePH₂, while Me₂PH₂I remains (Hofmann, B 4, 605) Formed also by heating chloroform with PH, I and ZnO (Hofmann, B 6, 302) with powerful odour May be condensed by 2 atmospheres' pressure at 0° Fumes in the air, and takes fire when gently warmed Feeble base, being absorbed by cone HClAq or cone. HIAq, producing crystalline salts, which are de composed by water into MePH, and the acid When passed into fuming HNO3 it yields methane phosphonic acid or methylphosphinic acid' MePO(OH), which forms crystals, v sol water, melting at 105° acid is not attacked by aqua regia. It yields the salts MePO₂Ba, MePO₂Pb, and MePO₃Ag, and the chloride MePOCl₂ [32°] (163°)

Salts — MePH, HCl four sided plates, very

volatile in the air, being dissociated - MePH2HI

D1-methyl phosphine C2H,P & 6 (CH3)2PH Mol w 62 (25°) Obtained by the action of caustic soda on its hydro iodide, which is obtained as above described (Hofmann, B 4, 610) Very volatile liquid which takes fire in the air May be oxidised to Me₂PO OH, a waxy solid, v sol water This acid melts at 76°, forms ciys talline Me₂PO OAg and is converted by PCl, into the chloride Me₂POCl [66°], (204°) This chloride is reconverted by water into the corresponding acid with less energy than MePOCl2 (Hofmann, B 5, 109, 6, 307)

Tri methyl phosphine C3H2P 28 P(CH3)3

Mol w 76 (41°)

Formation -1 By the action of MeCl upon calcium phosphide (Thénard, C R 21, 144, 25, 892) -2 From sodium or zinc phosphide and MeI (Cahours a Hofmann, A Ch [3] 41, 631, Chem Gaz 1855, 11) -3 From PCl, and ZnMe, (Hofmann a Cahours, C R 104, 29) -4 From PH_3 and MeI (Drechsel a Finkelstein, B 4, 354, Hofmann, B 4, 205, 430) -5 By heating CS₂ with PH₄I at 140° (Drechsel, J pr [2] 10, 180) 6 From phosphorus and MeI (Friedel a Silva, Wurtz's Dict 2, 938)

Preparation -By treating PCl, with ZnMe, in an atmosphere of CO2, decomposing the pro duct with caustic soda, and distilling in a very

slow current of hydrogen

Properties - Volatile oil with powerful nau seous odour, heavier than water Forms readily Unites readily soluble, crystallisable salts with halogens, oxygen, and sulphur With ClCH₂CO₂H at 100° it yields PMe₃Cl CH₂ CO₂H which forms the platinochloride (C, H12PO2)2PtCl. (Meyer, B 4, 734, C J 24, 1066)

Salts -B'2H,PtCl, orange yellow crystalline pp —B'₂PtCl₂ (Cahours a Gal, Z 1870, 662) Combines with CS₂ forming pale red crystals of PMe₃CS₂, which slowly changes, in ethereal solution, into PMe,S (Hofmann, A Suppl 1, 59)

Oxide PMe₃O [138°] (Collie, C J 53, 637) (215°) Formed by exposing PMe₃ to a slow current of dryair Deliquescent crystals Formed also, together with CH, by distilling PMe,OH Yields a platinochloride (PMe,O),H2PtCl, aq crystallising in orange plates or needles

Sulphide PMe₃S [105°] Obtained by gradually adding flowers of sulphur to PMe₃, or by distilling PMe, with cinnabar Not formed from the oxide and H2S or ammonium sulphide Four sided prisms (from concentrated aqueous solution) When warmed with a solution of a silver salt Ag₂S is deposited as a black mirror (Collie)

Selenide PMe, Se [84°] Formed from PMe, and selenium Blackens in the air, depositing selenium

Methylo-hydroxide PMe, OH Formed

by treating PMe,I with moist Ag₂O Caustic base, split up on distillation into PMe,O and

Methylo-rodide PMe,I Tetra methyl-phosphonium rodide Formed from PMe, and MeI (Hofmann a Cahours, A 104, 31) Formed also, together with PMe, by heating PH₄I (1 mol) with MeOH (3 mols) at 180° (Hofmann, B 4, 208) Silvery crystals

Methylo chloride PMe,Cl From PMe OH and HCl Deliquescent crystals, de composed by heat into PMc,HCl and ethylene (Collie, C J 53,637)—(PMe,Cl),PtCl, glisten ing yellow octahedra, insol water—PMe,AuCl,: brilliant yellow needles (from boiling water)

Methylo sulphate *(PMe4),SO, Formed from PMe4I and Ag2SO4 (Collie) Thick deliquescent needles Does not form an alum with Al (SO₄)₃ Above 300° it decomposes, giving quescent needles PMe,O and PMe,S

Methylo carbonate *PMe,O CO,H composes above 100° into PMe₃O, CO₂, and CH₄

(Collie)

Methylo acetate *PMe,OAc posed by heat chiefly into PMe O and acctone,

with traces of PMe, and MeOAc

Benzoate PMe, OB7 Formed by neutral ising a solution of PMe OH with HOBz (Collie, C J 53, 639) Deliquescent crystals, v sol water Decomposes between 250° and 300° almost completely into PMe,O and accto phenone

Ethylochloride PMe EtCl Obtained from PMe,EtI (Collie, C J 53, 718) Decomposes above 300° into PMe,HCl, PMe,EtHCl, and ethylene —(PMe,EtCl),PtCl, octahedra

Ethylo vodide PMe Etl Tri-methylethyl phosphonium woulde From PMe, and LtI in ether (Cahours a Hofmann, A 104, 33) Crystallises from boiling water Deliquescent, sol ether

Isoamylo nodide PMe, CH, I Deposited slowly from an ethereal solution of PMe, and CH₁₁I (Hofmann) Needles (from alcohol) Yields (PMe₃C₅H₁₁Cl)₂PtCl₄, crystallising from boiling water in splendid needles aggregated in spherules

Bromo ethylo-bromide C,H,,Br, 16, CH,Br CH,PMe,Br From PMe, and a large excess of ethylene bromide in alcoholic solution at 60° Trimetric prisms, abc = 5681 407 Hofmann, Tr 1860, 590) With Ag₂O it yields CH2(OH) CH2 PMe2OH whence the platino chloride (CH2(OH) CH2 PMe2Cl) PtCl, may be

Ethyleno dr-bromide (PMe,Br),Q,H, Formed from ethylene bromide and excess of PMe, at 100° Very deliquescent monoclinic crystals, $a \ b \ c = 1\ 054\ 1\ 1\ 126$, $\beta = 37^{\circ}49'$ Yields C.H.(PMe,Cl)2PtCl4, which crystallises from boiling HClAq in golden yellow laminar cessive treatment with moist Ag.O and HI forms C2H4(PMesI)2, crystallising in sparingly soluble needles

Tri-methyl-tri-ethyl-di-phosphine ethyleno-dibromide (PMe,Br)C,H,(PEt,Br) Formed from PMe, and CH,Br CH, PEt,Br Yields a caustic hydroxide and the platinochloride (PMe,Cl)C,H,(PEt,Cl)PtCl

Tetra-methyl-di-phosphine? P.Me, or (PMe2) s. (250°) Found among the products of the action of MeCl on calcium phosphide or of MeI on sodium phosphide (Thénaid, Hofmann a Cahours, A 104, 4) Liquid, with unpleasant odour, taking fire in the air Insol water Decomposed by HCl into PMe,, and a yellow pow-

der P.Me.(?

METHYL PHOSPHITE MeH,PO, Methylphosphorous acul Formed by gradually adding PCl₃ to methyl alcohol (Schiff, 4 103, 164) Acid syrup, resolved by heat into MeOH and phosphorous acid Its salts are slightly crys talline hygroscopic ma-ses, v sol water, sl sol alcohol, insol ether In aqueous solution they decompose, slowly in the cold, but rapidly on heating, into MeOH and metallic phosphites—Ba(MeHPO₃)—Ca(MeHPO₃), 2aq— Pb(MeHPO₃)

Tri methyl phosphite Me,PO, (185°) SG 1 1785 Formed from PCl, and NaOMe A 256, 281) The compound (Jachne, Me PO PtCl is formed by the action of McOH on PCl, PtCl (Schutzenberger Bl 2 18, 101 It crystallises in orange needles and

yıclds (Me,PÖ,) PtCl and (Me,PÖ,) PtCl N H METHYL-PHTHALIC ACID v lollenf di CARBOXYLIC ACID

Di-methyl phthalic acid & NIFNE DICARB OXYLIC ACID

Tetra methyl phthalic acid v IFIFA MLIHAL BENZENE I ICARBONNIIC ACII

METHYL-PHTHALIDE C H,O 1e

cale) Formed by reducing accophenene carb oxylic acid with sodium amalgam and acidify ing the resulting CO \n C,H, CH(OH) CH, (Ga briel a Michael B 10 2205, 20 2500) Thick oil soliditying below 0 Insol water and cold alkalis, v sol alcohol and ether sl sol liciom Boiling alkalis convert it into salts of the acid, which forms a crystilline silver salt CO Ag CoH, CH(OH) CH

Di methyl-phthalide $C_{ii}H_{ii}O_{i}$

 $C^{e}H^{4} < CO < O$ [650 (160°) at 25 mm, (271°) at 760 mm Formed by the action of zino dust and MeI on phthalic anhydride at 100° under a slightly increased pressure (Wis licenus, A 218, 361 Crystallises from ether in large crystals which are doubly refracting

Reactions -1 Converted by the action of cone KOHAq into the k salt of o oxy iso propyl benzoic acid -2 Sodium amalgam yields the

dihydride $C_eH_{\bullet}C_{CH(OH)}^{Ve}>0$ [90°], a yellow amorphous powder, insol water, sol alcohol and ether, which reduces Tehling's solution and ammoniacal AgNO3 -3 Reduction with HI yields o iso propyl benzoic acid - 4 Potassium cyanide at 250° forms o propenyl benzoic acid CH, CMe C,H, CO H [61°]
METHYL PHTHALIMIDE v

Methylimide

of PHTHALIC ACID

METHYL-PHTHALIMIDINE C.H.NO s.e $C_{\bullet}H_{\bullet} < CO$ [120°] (300°)

Formation -1 By reducing methyl phthalamide $C_eH_4 < \stackrel{OO}{CO} > NMe$ with tin and HClAq(Graebe, A 247, 303) -2 By heating a solution

of MeI for 6 hours at 100° (Barbier, C. R 107, 918) -3 By heating phthalide with alcoholic methylamine for 12 hours at 220° (B)

Properties -Slender needles or plates, v sol water, alcohol, and ether Oxidised by KMnO, to methyl phthalimide and, finally, to phthalic Combines with bromine (C₉H₉NO) Br₆, crystallising in needles [150°]

Salts —Hydrochloride [120°] Prisms B',HAuCl, yellow prisms, sl sol cold water

a METHYL HOMO o PHTHALONITRILE v

o Cyano phenyl propionitrile
METHYLPIASELENOL v Organic Selenium

METHYL PIAZTHIOLE C, H, N, S 1 e

 $\begin{bmatrix} 3 & 6 \\ 5 & \end{bmatrix} C_0 H_2 Me$ S [34°] (234°)

(by Rioult's method) 143 (calc 150) Formed by heating tolylene o diamine with H2SO, at 180° (Hinsberg, B 22 2900) Yields a per nodide when treated with I in HIAq Br in CHCl, forms CHBiNS which crystallises in white needles 1980 A mixture of cone HSO, and HNO, forms CH (NO,)NS crystallising in colourless needles [156°]

Salt -B H PtCl. reddish yellow crystals,

decomposed by water METHYL PIPECOLINE v DI METHYL PYR IDINI HEXAHYDRID

METHYL PIPERIDINE v METHYL PARIDINE

HE VAHY DRIDE

METHYL PROPARGYL-AMINE C.H N 16 CH, NH C C CH, Formed by the action of MeI on propargylamine in alcoholic solution (Paal a Hermann, B 22, 3083; Very volatile yellowish liquid, with ammoniacal odour -B'HI (noups of long hygioscopic needles -B H2C O4 Slender white needles, sl sol alcohol [141

METHYL-PROPIONIC ACID v BUTYRIC ACID

METHYL PROPYL ACETAL v ALDFHYDE METHYL PROPYL ACETIC ACID v HEXOIC

METHYL PROPYL-ACETOACETIC ETHER

ACFTOACETIC ACID

METHYL ISOPROPYL-ACETONE v METHYL ISOANYL KETONE

DI - METHYL - PROPYL - ALKINE v Dr-METHAL OXYPROPYL AMINE

DI METHYL ISOPROPYL - ALLYL . CAR. BINOL : ENVENYL AI COHOL

TRI METHYL PROPYL AMMONIUM

IODIDE NMe, PrI Propylo woded of trimethylamine [190°] Formed by heating propylamine with alcoholic NMe, (Langeli, G 16, 385) Long needles Yields crystalline NMe, PrCl and (NMe,PrCl),PtCl, The hydroxide NMe,PrOH is decomposed by heat into propylene and NMe.

METHYL-PROPYL ANILINE C₁₀H₁₃N : 6. C₄H, NMePr (212° uncor) Liquid Prepared by the action of methyl iodide upon propylannline Claus a Hinzel, B 19, 2785, cf Nolting, J 1883, 702) -B'HCl very hygroscopic crystals, [106°]

Ethylo-rodide > Propylo wodide METHYL-

ETHYL-ANILINE METHYL-PROPYL-BENZENE v CYMENE

s Methyl di-propyl benzene C13H20 of phthalimidine in aqueous KOH with excess [C.H.,Me(C.H.),1[1 3 5] (248°-248). Formed by the action of H₂SO₄ on a mixture of acetone and methyl n propyl ketone (Jacobsen, B 8, 1259) Yields uvitic acid on oxidation with dilute

s-Di methyl propyl-benzene C,,H, C₆H₂Me₂C₃H₂[13.5] (206°-210°) Formed by the action of H₂SO₄ (3 vols) on a mixture of acetone (4 vols) and methyl propyl ketone (2 vols) (Jacobsen, B 8, 1259) Oxidised by boiling dilute HNO, to mesitylenic acid

u-Di-methyl-propyl-benzene C11H16 C₆H₈Me₂Pr [1 4 2] (206°) Formed from bromop-xylene, propyl bromide, and sodium (Uhlhorn, **B** 23, 2350) Liquid, not solidified at -20° Yields a tri nitro derivative [85°], and a tri-

bromo- derivative [49°]

Sulphonic acid C.H.Me.Pr SO.H Salts -BaA'₂. -NaA' 1 aq -Amide C₆H₂Me₂Pr SO₂NH₂. [125°] Anilide C.H.Me.Pr SO2NHPh [216°]

u-Di-methyl-propyl-benzene C_eH₃Me₂Pr[1 3 4] (208°) Formed from bromo-m-xylene, propyl bromide, and Na (Uhlhorn) Liquid, not solid at -20° Yields a tri-nitro derivative [110°] and a tri-bromo-derivative [39°] May be oxidised to (1,3,4) di-methylbenzoic acid

Sulphonic acid C₆H₂Me₂Pr SO₃H Groups of needles — Salts — NaA'4\2aq — BaA'2 2aq — MgA'2 5aq — Amide C₆H Me,Pr SO₂NH, [102°] — Anilde C₆H,Me,Pr SO₂NHPh [c 182°]

u-Di methyl-propyl benzene

C.H.Me.Pr [1 2 4] (209°) Formed from bromoo-xylene, propyl bromide and sodium (Uhlhorn, B 23, 2349) Liquid, not solid at -20° Yields oxidation (1,2,4) di methyl benzoic [162°]

Sulphonic acid C₆H₂Me₂Pr SO₃H Thin needles — Salts — BaA'₂ $3\frac{1}{2}$ aq - Amıde $C_0H_2Me_2Pr$ SO₂ NH_2 [124°] -Anılıde Č,H,Me,Pr SO,NHPh [214°].

u Dı methyl-ısopropyl benzene C₆H₃Me₂Pr [1 3 4] (194°) Formed from bromo m-xylene, isopropyl bromide, and sodium (U) Liquid Yields a tri-bromo-derivative [261] and a tri-nitro-derivative [182°]

C₆H₂Me₂Pr SO₃H. Sulphonic acid Needles —Salts —NaA' 4aq —BaA'2. [163°] Amide C.H.Me,Pr SO,NH, Anılıde C.H.2Me,Pr SÖ2NHPh [207°]

METHYL-PROPYL-BENZOIC ACID C11H14O2 C₈H₃Me(C₈H₇)CO₂H Carbocymolic acid Obtained from its nitrile, which is pro duced by distilling potassium cymene sulphonate with KCy (Paterno a Fileti, B 8, 442, Paterno a Spica, G 9, 400)

Amide C₆H₃Me(C₃H₇) CONH₂. [139°] Obtained by boiling the nitrile with alcoholic potash Needles, sl sol cold water

METHYL-PROPYL-CARBINOL v Sec-amyl ALCOHOL

Di-methyl-propyl-carbinol . Tert-HEXYL ALCOHOL:

Methyl-di-propyl-carbinol v OCTYL ALCOHOL. METHYL PROPYL CARBONATE C,H,O, s.e CH,O CO OC,H,. (131° cor) SG 21 978 (Röse, A 205, 230)

METHYL-PROPYL-COUMARIN C, H, O, s &. CH CH (2) [53°] (220°-230°). ∙O – ĊO (8)

Formed by nearing a man a Welsh, B 11, and and H₂SO, (Pechmann a Welsh, B 11, white needles V sol alcohol, Formed by heating a mixture of thymol, malic ether, benzene, acetic acid, and chloroform, v sl sol water

METHYL PROPYLENE 4 THIO-UREA

C NHMe Methyl amido - methyl ĊH, N thiazole dihydride [50°] Formed by the action of methyl thiocarbimide on \$6 oxy propylamine (Hirsch, B 23,971) Long needles (from ligroin), Its aqueous solution is strongly v sol water alkalıne —B',H PtCl, [143°] Large dark-red needles (from hot water) — B'C,H2(NO2),3OH [145°] Needles — Compound with methyl throcarbimide B'MeNCS [64°] White

columns (from MeOH) Methyl propylene w thio-ures C3H10N2S 2.6 CHMe S

C NH Imido - dr methyl - thrazole CH₂ NMe tetrahydride Formed from propylene \(\psi \) thiourea, MeI, and KOH (Gabriel, B 22, 2989) Converted by bromine water into the acids NHMe CH, CHMe SO, H [220°-228°] (CONH, NMe CH, CHMe SO, H [230°-240°] METHYL PROPYL-ETHANE v HEXANE

METHYL ISOPROPYL FLUORENE C., H.

Retene fluorene C.H.MePr [6 5 1 4]

[97°] Formed by passing the vapour of methyl isopropyl di phenylene ketone (retene ketone) through a red hot tube (Bamberger a Hooker, A 229, 142) Formed also by heating this ketone with HIAq and phosphorus in sealed tubes White plates, v sol cold ether, hot alcohol, and In the fused state, or in alcoholic solu tion, it exhibits violet fluorescence It yields a di nitro derivative [245°]

METHYL ISOPROPYL FLUORENE ALCO $C_{\theta}H_{\bullet}$

HOL C17H18O 1 e CH(OH) [134°] C.H.MePr

Formed by the reduction of methyl isopropyl di phenylene ketone (Bamberger a Hooker, A 229, 144) White needles, insol water, v sol alcohol and ether Readily oxidised back to the one The acetate melts at 71°
METHYL PROPYL GLUTARIC ACID

CO.H CHPr CH. CHMe CO.H [102°] Formed from sodium propyl-malonic ether and bromo isobutyric ether, the product being saponified, and the resulting (CO,H), CHPr CH, CHMe CO,H [168°] being decomposed by heat (Bischoff, B 23, 1940) White aggregates of crystals (from petroleum-ether)

DI METHYL-PROPYL GLYCOLLINE v Di-METHYL DI-OXY PROPYL-AMINE

METHYL PROPYL-GLYOXALINE C,H,2N, NPr CH Oxal - propyl - sthylins. N — ČH

(225°). SG 9641 Formed by the action of propyl bromide on methyl glyoxaline (glyoxalsethyline) (Radziszewski, B 16, 489) Colourless liquid

Methyl-propyl-glyoxaline Pro NMe CH

Oxal-methyl-butyline (215° at 722 mm) S G
29 985 From propyl glyoxaline and Mel
(Rieger, M 9, 606) Oil, v sol alcohol, ether,
and chloroform—B'H.PtCl, orange red prisms

METHYL PROPYL-GLYOXAL v METHYL-

PROPYL-DIKETONE

DI-METHYL PROPYLIDENE DIKETONE C.H.₂O₂ ie (CH₂CO)₂CHEt Ethyl-acctyle acctone (179°) Prepared by heating the sodium derivative of methylene di methyl diketone with Eti at 140° (Combes, A Ch [6] 12, 248, C R 104, 920) Colourless liquid with pleasant odour, sl sol water, miscible with ether, alcohol, and chloroform Decomposed by potash into CH₂CO₂K and CH₂CO CH₂Et Combines with NaHSO₄ Sodium yields (CH₄CO)₂CNaEt which reacts with alkyl iodides

METHYL PROPYL KETONE C.H., 0 1e CH, CO C.H., Ethyl acetone (102°) S G 17 8124, 32 8044 (Perkin, C J 45, 479), 22 805 (F a D) H F p 72,410 H F v 69,400 (Thom sen, Th) M M 5 499 at 16 1° (P) Formation—1 Rv dot: 11

Formation—1 By distilling calcic acetate (48 g) mixed with calcic butyrate (65 g), and rectifying the product The yield (10 g) is small (Semljanitzin, J pr [2] 23, 263, cf Friedel, A Ch [4] 16, 366, A 108, 124, Grimm, A 157, 251)—2 By boiling ethyl acetoacetic ether with potash or baryta (Frankland a Duppa, A 138, 216)—3 By the action of ZnMe., fol lowed by water, on butyryl chloride (Butlerow, Bl [2] 5, 17)—4 By the oxidation of sec n amyl alcohol (Wurtz, A 148, 133, Schorlemmer, C J 25, 1085, A 161, 269, Wagner a Saytzeff, A 179, 322)—5 By the action of water and HgBr₂ on valerylene (hutscheroff, B 14, 1542)—6 By the action of kOH on (CH, CO)₂CHEt (Combes, A Ch [6] 12, 248)

Properties—Liquid, v sl sol water Combines with hydrogen sodium sulphite, forming C_bH₁₀(OH)SO_sNa jaq (Gimm) Reduced by means of sodium amalgam to see amyl alcohol CH₂CH(OH) CH_Et (119° cor) (Belohoubek, Sitz W [2] 74, 80) and a pinacone C₁₀H₁₂O (225°-230°) Yields acetic and propionic acids on oxidation (Schorlemmer), Wagner obtained butyric acid (Bl [2] 38, 264) PCl₂ forms CH₂CCl₂CH_Et, whence alcoholic potash produces CH·CCH_Et, and this is converted by alcoholic potash at 170° into CH₂C CEt (56°) (Favorsky, J R 1887 414) CH₂CCl₂CH_Et is split up on distillation into HCl and C₂H₂Cl (c 95°) Amyl nitrite and HCl or NaOEt forms the mitroso-derivative C₂H₂CO CH NOH [48°-51°], which is also an oxim of propyl-glyoxal From this oxim may be prepared the compounds C₂H₂C(NOH) CH(NOH) [168°] and C₂H₂C(N₂HPh) CH(N HPh) [168°] (Claisen a. Manasse, B 22, 528)

Manasse, B 22, 528)

Oxim C.H. C(NOH) CH. Oil Converted by gaseous HCl in HOAc at 100° into propylamine and acetic acid (Beckmann, B 20, 2580)

Methyl isopropyl ketone C₂H₁₀O v.e CH₂CO CH(CH₂), Di methyl acetone 'Amyl ene oxude' (94°) S G 2 822, 12 805 (Winogradoff), 12 810 (F a D) C E $(0^\circ-18^\circ)$ 00118

Formation —1 By the action of baryta water on di methyl aceto acetic ether (Frankland a Duppa, Pr 14, 463, A 138, 332) —2 By the dry distillation of a mixture of calcium iso butyrate and calcium acetate (Munch, B 7, 1370, A 180, 327) —3 By the action of tin and HClAq on di nitro heptoic acid, which is one of the products of the action of nitric acid on camphor (Kachler, A 191, 162) —4 From amylene glycol (CH₂)₂C(OH) CH(OH) CH₂ by dehydration with P₂O₃ (Flavitzky, B 10, 2240) —5 From (CH₂)₂CH CH(OH) CH₂(OH) by dehydration with P₂O₃ (Flavitzky, B 10, 2240) —5 From (CH₂)₂CH CH(OH) CH₃, by heating with dilute HCl at 100°, and treating the product with potash (Bauer, C R 51, 55, A 115, 91, Eltekoff, J R 14, 358) —7 By shaking (CH₂)₂CH CCH with diluted H.SO₄ (S G 164) (Flavitzky a Kryloff, J R 10, 347) —8 By cylaising Me CH(OH) Pr by CrO₃ (Winogradoff, A 191, 133) —9 By heating (CH₃)₂CBr CHBr CH₄ with water and PbO at 150° (Eltekoff, J R 10, 215), or by digesting it with water alone (Niederist, A 190, 300, Nageli, B 10, 2983) —10 By heating Me CH(OH) Pr with excess of dilute (1 pc) H SO₄ at 100° (Kondakoff, J R 17, 300)

Properties—Liquid Gives the iodoform re action with iodine and potash inne compound with NaHSO, On oxidation it yields acetone and acetic acid, and inally CO, and acetic acid

Oxim CH, C(NOH) CHMe. (158°) From the ketone and hydroxylamine (Nageli, B 16, 2984) Formed also by heating the oxim of dimethyl acetoacetic acid above 97° (Wallach, A 248, 178)

Reference - Chloro methyl isopropyl KE

Methyl propyl diketone C₄H₁₀O₂: e CH₃ CO CO CH₂ CH...CH₃ Acetyl butyryl (128°) S G ¹² 9343 Obtained by boiling its mono oxim with dilute H₂SO₄ (Von Pechmann, B 21, 2140) Yellow oil, with irritating odour like quinone

Mono oxim CH, CO C(NOH) C₂H, Isoni troso propyl action: [49 5°] Formed by the action of nitrous acid on propyl acetoacetic ether (Treadwell, B 14, 2159) Large plates With phenyl cyanate it reacts with formation of CH, CO CPr NO CO NHPh [93°] (Goldschmidt, B 22, 3108), whence hydroxylamine yields CH, C(NOH) CPr NO CO NHPh [129°-131°]

Di - oxim CH, C(NOH) C(NOH) C,H Methyl propyl glyoxim [168°] Formed by the action of hydroxylamine hydrochloride in aque ous alcoholic solution on isomitroso propyl ace tone (Schramm, B 16, 2185) Small needles With phenyl cyanate it reacts with formation of CMe(NO CO NHPh) CPr(NO CO NHPh), crystal lising in pearly plates [164°-170°] (Goldschmidt a Strauss, B 22, 3108)

Oxim phenyl hydrazide C₁.H₁,N₁O ie CMe(N₂HPh) CPr(NOH) [130 5°] Formed by the action of phenyl-hydrazine acetate on the mono oxim (Otte a Pechmann, B 22, 2121) Needles, sl sol dilute NaOHAq Gives a violet colour with H₂SO₄ and FeCl₂

(a)-Phenyl-hydrazide $C_{12}H_{16}N_2O$ Formed by the Me C(N, HPh) COPr [114°] action of phenyl hydrazine on the diketone (O a P) Insol water and ligroin, v sol alcohol and ether With conc H SO, and FeCl it gives a red colour

C, H,6N O (β)-Phenyl hydrazide Me CO C(NaHPh) Pr [109°] Formed from propyl acetoacetic acid by the action of diazo benzene chloride in presence of NaOAc (Japp a Klingemann, A 247, 220) Colourless needles

(from benzene and ligroin)

Dr phenyl-dr-hydrazide C₁₈H N₄ re Me C(N,HPh) C(N₂HPh) Pr [136 5°] Formed Me C(N.HPh) C(N₂HPh) Pr [136 5°] Formed as a yellow pp when excess of phenyl hydrazme Formed acetate is added to the ketone, its phenyl hydra zide, or its oxim phenyl hydrazide (Otte a Pechmann, B 22, 2121) Yellow needles (from benzene), more easily soluble than its homo logues with fewer atoms of carbon in the mole

Methyl isopropyl diketone C₆H₁₀O₂ i e CH₃ CO CO CH(CH₃), Acetyl isobutyryl (116°) Formed by boiling its oxim with dilute H SO, (Von Pechmann, B 21, 2140, 22, 2122) Yellow liquid, with irritating odour, sl sol water

Oxim CH, CO C(NOH) CHMe Isonitroso methyl isobutyl ketone [75°] Formed by the action of nitrous acid on isopropyl acetoacetic ether (Westenberger, B 16, 2991) White plates, sol alcohol, ether, alkalis, and hot water

METHYL PROPYL-KETONE CARBOXYLIC

ACID v Ethyl ACETOACETIC ACID

Methyl-propyl-ketone tricarboxylic acid CH₃ CO CH(CH, CO H) CH(CO H) B acetyl glutaric acul [121°-124°] The til ethyl ether is formed by the action of chloro or bromo lævulic (acetyl propionic) ether upon sodio malonic ether Colourless crystalline solid At 160° it splits off CO, giving acetoglutaric acid The neutral NH, salt gives pps with AgNO₈, BaCl₂, and Pb(OAc) The zinc salt is a very soluble amorphous solid

Tri ethyl ether A"Et, (Conrad a Guthzeit, B 19, 43) (285°-295°), oil

METHYL - ISOPROPYL - KETONE - CARB OXYLIC ALDEHYDE Dr-oxim C. H. N. O. 1 e CH₂ C(NOH) CH₂CMe CH NOH [90°] Formed from di methyl pyrrole and hydroxylamine (Ciamician, B 23, 1788) Small needles or prisms, v sol alcohol, and water, sl sol ether Reduces Fehling's solution Sodium reduces it in alcoholic solution to di methyl tetra methylene-

METHYL PROPYL-DI-KETOXIM v Oxim of METHYL PROPYL DIKETONE

METHYL ISOPROPYL MALONIC ACID

C,H,2O, ie CO2H CMePr CO2H [1249] Formed by saponifying its ether (Van Romburgh, R T C 5, 236) Crystallises from benzene Split up at 150°-200° into CO₂ and a hexoic acid Salts —CaA'₂ V sol water —AgA' white Split up

Salts - CaA'2

Ethyl ether Et,A" (221°) SG'15 990 Formed from sodio malonic ether, MeI, and PrI Colourless liquid with agreeable odour

METHYL PROPYL OXIDE C4H10O 2 e CH, OPr (389°) SG 2 7471 SV 1051 CE (0° to 10°) 00146 (Dobriner, A 243, 2, cf Chancel, A 151, 305)

METHYL-PROPYL PHENOL & CARVACRCL, CYMENOL, and THYMOL

Tetrahydride v Borneol and Cineol.

DI METHYL PROPYLPHENYL AMINE

C,H,(C,H,) NMe Di methyl phenpropyl amine (230° uncor) Formed by the action of sodium on a mixture of propyl bromide and di methyl p bromo aniline (Claus a Howitz, B 17, 1327). Colourless oil

Methylo rodide B'MeI [168°], plates METHYL ISOPROPYL PHENYL CARB-AMINE v Iso CYMYL CARBAMINE

METHYL PROPYL PHENYLENE DIAMINE CoH Me(C3H7)(NH) Formed by reducing the di oxim of thymoquinone with tin and HCl (Liebermann, B 18, 3193) Oxidised by CrO, or FeCl, to thymoquinone -B"H,Cl needles

METHYL ISOPROPYL DIPHENYLENE KE- C_bH_4

TONE C17H18O 2 e CO Retene-`Ċ_°H Me(C**,H**,)

ketone [90°] Formed by oxidising retene glycolic acid C₁₀H₁₆ C(OH) CO H (Bamberger a Hooker, A 229, 136) I ormed also from retene quinone by the action of alkaline KMnO4 or by passing it over ied hot Ba(OH), or PbO (Γk strand, B 17, 692) Yellow prisinatio needles or rectangular trimetric plates (by spontaneous evaporation), v sol ligioin, benzene, chlorofoim, alcohol, and HOAc Volatile with steam and with vapour of alcohol Does not react with hydroxylamine or with NaHSOs Reacts with phenyl hydrazme Reduced by sodium amal gam to methyl isopropyl fluorene alcohol (q i), and by red hot zinc dust to methyl isopropyl fluorene

METHYL ISOPROPYL-PHENYL ETHYL GUANIDINE v Iso CYNYL ETHYL GUANIDIN

METHYL PROPYL PHENYL GLYOXYLIC ACID C₁₂H₁₄O, ie [2 5 1] C₆H₃MeP₁ CO CO H Formed by oxidising the ketone C. H. McPi CO CH. with cold aqueous KMnO4 (Claus, B 19, 233) Thick oil, easily decomposing into CO, and C.H, MePr CHO Dilute nitric acid yields C₆H₃Me(CO₂H)₂

METHYL PROPYL PHENYL METHYL KE TONE C12H16O re C8H3MePr CO CH3 (248°) Formed from cymene, AcCl, and AlCl, (Claus a Cropp, B 19, 232)

METHYL ISOPROPYL - PHENYL - THIO-ETHYL-UREA v Iso CAMYL ETHYL THIO UREA DI METHYL-DI ISOPROPYL DI-PHENYL-

THIO-UREA v Di iso CYMYL THIO UREA

METHYL - ISOPROPYL - PHENYL UREA & ISO CYMYL UREA

METHYL - ISOPROPYL - PHENYL - URE THANE v Iso CIMYL CARBAMIC ETHER

METHYL ISOPROPYL-PHOSPHINE C.H.,P v.e CH₃ PH C₃H, (79°) Obtained by heating isopropyl phosphine with MeI at 100° (Hof mann, B 6, 299)

DI-METHYL-DI-PROPYL PYRAZINE

 $C_{12}H_{20}N_2$ to $N \leqslant \stackrel{\hbox{\scriptsize CMe CPr}}{\hbox{\scriptsize CPr CMe}} N$ Di - propul -(233°-245°) Prepared by the reduction of the oxim of methyl propyl diketone (nitroso methyl-butyl ketone) with tin and HCl (Treadwell, B 14, 1461, 2160, Oeconomides, B19, 2526) Oil, with narcotic odour, turning brown in the air -B'₂H₂PtCl₆ red octahedra, si sol water —B'AgNO, aq crystals, insol cold

METHYL-PROPYL-PYRIDINES Parvoline The base obtained by the action of P2O5 on a mixture of propionic aldehyde and acetamide (Hesekiel, B 18, 3097) has been shown by Durkopf a Göttsch (B 23, 685) to yield pyridine tricarboxylic acid on oxidation, and must there fore be dimethal ethyl paridine $(q \ v)$ volines, which must be C HMe, N, C, H, Me(C,H,)N, C.H.Me EtN, or C H.Et.N, occur in crude paraf fin oil (Williams, C J 7,97), in coal tar (Thenius, J 1861, 502), in the product of the distillation of cinchonine with kOH (Oechsner de Coninck, Bl [2] 34, 214), and in putrid flesh (Gautier, Bl 48, 11)

Di methyl-propyl pyridine C₁₀H₁₅N i e C₃H₂NMe Pr (1 3 2) n Propyl lutidine idine (c 195°) at 718 mm Formed by distilling potassium di methyl propyl pyridine dicarboxyl ate with lime (Jæckle, A 246, 37) Colour less liquid, sl sol water, v sol alcohol and ether Its hydrochlouide is crystalline -B'₂H₂PtCl₆ [185] Isomeride v Coridine

ν Methyl-isopropyl pyridine hexahydride CH CH CHPr NVe

SG 2 8593 I ormed by adding the calculated quantity of MeI to a solution of isopropyl pyridine hexahydride in MeOH, evaporating and distilling the residue with potash (Laden burg A 247, 77) Oil, smelling like conine — B HAuCl, [131] B H.PtCl, [100°] Plates, sl sol water — Plates, v sol water and alcohol, insol ether -Picrate B'C, H (NO), OH

Di-methyl-propyl-pyridine hexahydride

C₁₀H₂₁N 1 e CHPr CH CHMe NH Propyllupetidine (c [180°]) at 718 mm Obtained by reducing di methyl propyl pyridine in alcoholic solution with sodium (Jaeckle, A 246, 46) Colourless oil Gives a brownish pp with FeCl3 and a yellowish pp with MnSO₄—B' H₂PtCl₆ [197°] Orange stellate needles

DÍ METHYL PROPYL PYRIDINE DICARB OXYLIC ACID C, H, NO, 1e

CPr < $< C(CO_2H)$ < CMe > (247°) Formed by sa ponifying its ether, which is obtained by oxida tion, with nitrous gas, from the product of the action of ammonia on butyric aldehyde mixed with acetoacetic ether (Jaeckle, A 246, 36) Colourless prisms (containing aq) When anhy drous it melts at 247°, but at 212° when hydrated V e sol hot, m sol cold, water Yields di methyl propyl pyridine when distilled with lime

Ethyl ether Et,A" (308°) at 715 mm Light yellow oil Saponified by boiling first with aqueous, and then with alcoholic, potash -

aqueous, and then with alcoholo, potash-(C₁₆H₂₁NO₁)₁H₂PtCl₆ [187°] Orange prisms Dihydrids of the ethyl ether CHPr C(CO₂Et) CMe NH [118°] Forme Formed by condensation of butyric aldehyde with aceto acetic ether and ammonia (Jaeckle, A 246, 34) Yellowish white prisms, v sol alcohol and ether, msol water

dicarboxylic Di methyl isopropyl-pyridine

other. Dehydride

CHPr CC(CO₂Et) CMe NH [97°] Formed by the action of alcoholic ammonia on a mixture of isobutyric aldehyde and acetoacetic ether (Engelmann, A 231, 47) Long prisms (from 90 p c alcohol) Oxidised by nitrous acid, in presence of alcohol, to di methyl pyridine dicarboxylic ether C.HMe N(CO Et)

METHYL DI ISOPROPYL QUINOLINE DI HYDRIDE C₁₆H₂N (299°) Formed by heat ing di iso propyl indole with MeI and MeOH (Dennstedt, B 21, 3437) [177²⁷ Oil -B'.H.PtCl.

METHYL PROPYL-STYRIL KETONE

C₁,H₁,O i e C₆H₄(C₂H₂) CH CH CO CH₂ Cu minal acetone (181° at 23 mm) Formed by the action of dilute (10 pc) NaOHAq upon a mix ture of cuminic aldehyde (20 g), acetone (20 g), water (300 g), and alcohol (170 g) (Claisen a Ponder, A 223, 147) Yellow oil

METHYL ISOPROPYL SULPHIDE C.H., S 14 MeSP1 (93°-95') VD 4502 Formed by dissolving sodium in an ethereal solution of isopropyl mercaptan, and slowly adding MeI to the product (Obermeyer, B 20, 2923)

METHYL PROPYL DITHIOCARBONATE

MePiCS O Methyl propyl xanthate 1 084 (Nasını a Scala, G 17, 66)

S METHYL PROPYL THIO-UREA C,H,2N28 [79°] Prepared from e CH, NH CS NHC, H methyl thiocarbimide and propylamine, or from propyl thiocarbimide and methylamine (Otto Hecht, B 23, 284) Transparent glassy plates (from very dilute alcohol), sl sol cold water, m sol hot water, v sol alcohol and wood spirit, extremely sol acetone and chloroform, v sol ether benzene, and Co, v sl sol warm light petroleum

DI METHYL PYRAZINE C.H.N. 1 e

N ≪CMe CH CH CMe Ketine Di methyl aldine (Meyer, B = 21 - 19) $(170^{\circ}-180^{\circ})$ Formed by reduction of nitroso acetone with tin and HCl (Treadwell a Steiger, B 15, 1059, 1055 Oeco nomides B 19,2526 Wolff, B 20,433) Formed also by heating its dicarboxylic acid Oil, with alkaloidal odour - B H PtCl. golden plates, sol hot water

Tetra methyl pyrazine O₈H₁₂N₂ i e

N CMe CMe N Methyl ketine Di methyl .86°1 Letine Tetra methyl aldını Formed by reducing with tin and HCl the oxim of di methyl diketone (methyl nitroso ethyl ketone) CH, CO C(NOH) CH, (Gutknecht, B 13, 1116, Treadwell, B 14, 1469, Biaun a V Meyer, 21, 1947) An intermediate base appears to be C.H.N (Braun, B 22, 556) Tetra methyl pyr azine is also formed, together with CO2 and other products, by heating CH, CO CHBr CH, CO, H or CH, CO CH(OH) CH, CO, H with cone NH, Aq (Wolff, B 20, 427) Glistening prisms (anhy drous) or long white needles (containing 3aq) Very volatile Melts at 74°-77° when hydrated, but at \$6° when anhydrous Strong character istic smell V sol alcohol and ether By al kaline KMnO, it is oxidised to pyrazine tetra carboxylic acid C₄N₂(CO₂H)₄ Salts — B"HCl 2aq

easily soluble, [91° anhy]—B",H,Cl,PtCl, red glistening needles. -B"H,Cl,PtCl, 4aq orange red needles.

Methylo-rodide B"MeI [216°] anhy Yellow needles (containing 2aq), v sol water and alcohol, msol ether

Methylo chloride B"MeCl [c 105°], needles -B"MeClHClPtCl, aq orange red pyra mids (from hot water)

DI METHYL PYRAZINE DICARBOXYLIC $N < C(CO_2H) CMe > N$ ACID C.H.N.O. ı e.

Prepared by saponification of its ether, which is formed by reducing nitroso acetoacetic ether with stannous chloride (Wleugel, B. 15, 1050) Formed also by oxidising di methyl diethyl pyrazine by aqueous KMnO₄, and by condensation of imido oximido butyric ether CH₂ C(NH) C(NOH) CO₂Et by warm ZnCl (Oeconomides, B 19, 2524)

Properties - Colourless crystals (containing 2aq), melting at 201° when anhydrous alcohol and acetone, m sol hot water and tolu ene, nearly insol ether, benzene, and ligroin Decomposes when heated above 200° into CO₂

and di methyl pyrazine

Salts - BaA"3aq glistening crystals -*K₂A" slender felted needles Gives amorphous pps with FeCl₃ and CuSO₄ -Ag A" yel lowish white pp

(316° cor) Ethyl ether Et2A" [86°

Long colourless needles, sol alcohol

METHYL-PYRAZOLONE OXY METHYL PYRAZOLE

(a)-METHYL PYRIDINE C, H, N 1 e

N CMe CH CH CH (a) Picoline Mol w 93 (129°) (L), (133 4° coı) (Thorpe, $C\ J$ 37, 223) S G $\frac{9}{4}$ 9656 (L), 9616 (T) C E (0°-10° 000975, (0°-100°) 0010968 (T) S V 111 5 C E (0°-10°) S V 111 5

Occurrence - In bone-oil (Anderson, A 60, 86, Weidel, B 12, 2008), where it is mixed with a little (3) picoline and di methyl pyridine (La denburg, B 18, 49) It is also the chief con stituent of coal tar picoline (Goldschmidt a

Constam, B 16, 2976)

Formation -1 By heating pyridine (a) carb oxylic acid with fuming HIAq at 260°, or by treating the acid with zinc and HOAc (Seyfferth, J pr [2] 34, 244) -2 By the action of aldehyde on aldehyde ammonia (Durkopf a Schlaugk, B 21, 297) -3 By heating pyridine methylo iodide in sealed tubes at 300° (Ladenburg, A 247, 7, C R 103, 692)

Preparation - Crude pyridine (50 g boiling between 128° and 134°) is dissolved in HClAq (170 g of 11 pc), and a hot solution of HgCl₂ (312 g) in water (41 litres) is poured in The double salt crystallises out, and, after recrystal lisation, is decomposed by aqueous NaOH (La

denburg, A 247, 6)

Properties - Liquid, mactive to light, miscible with water and alcohol Picoline lessens the heart's action, and acts on the nervous sys tem somewhat like nicotine (Oechsner, Bl [2] 38, 547)

Reactions -1 Yields pyridine (a) carboxylic (picolinic) acid on oxidation (Weidel) -2 When heated with sodium it yields di methyl dipyridyl 3 Methylal and ZnCl₂ yield CH₂(C₂H₆N)₂.—4 Chloral forms C₅NH₄ CH₂ CH(OH) CCl₂ [87°], the hydrochloride of which C₅H₅NOCl₂HCl melts Alcoholic potash converts it into pyridyl acrylic acid (Einhorn a Liebrecht, B 20.

1592) —5 Paraldehyde at 260° forms allyl pyr idine C.NH, C.H. (190°), S G 2 9595 (Laden burg, A 247, 26) Its aurochloride melts at 136°, its platinochloride at 186° Allyl pyridine is reduced in alcoholic solution by sodium to conine —6 Furfuraldehyde and a little ZnCl₂ at 170° yields C₂H₄N CH CH C₄H₂O [58°] (Merck, B 21, 2709), v Furfuryl vinyl pyridine In alcoholic solution it is reduced by sodium to the hexahydride of furfuryl ethyl pyridine (q v) 7 Glycolic chlorhydrin at 140° forms a compound $C_8H_{11}NO$, which yields the salts $B'_2H_1PtCl_6$ [200°] and $B'HAuCl_4$ [100°] (Alexander, B 23, 2714)

Salts -B'2H2PtCl6 aq [178°] Monoclinic tables or prisms, sl sol water —B' H2PtCl, 2aq (Weidel) — B',H,PtCl₆ [195°] Monoclinup plates, a b c = 6636 1 9078, β = 72° 46′ (Stohr, J pr [2] 42, 420) -B'HAuCl, [168°] Needles, d pr [2] 22, 240) — D LINGO, 1 [10] Prisms (from dilute HClAq), v sl sol cold, v sol hot, water — B',ZnCl₂ (at 120°) Crystals (from alcohol) (Lachovitch a Bandrowsky, M 9, 517)

Picrate B'C₆H₂(NO_.)₃OH [165³] water (Lange, B 18, 3436)

(a) Methyl pyridine tetrahydride C₈H₁₁N i c NH CMe CH CH Formed by the action of alcoholic NH, upon methyl ω brome butyl ketone, probably by elimination of water from the intermediate CH, CO CH, CH, CH, CH, NH, (Lipp, B 19, 2843)

(a)-Methyl pyridine hexahydride CaH12N 1 e NH CHMe CH CH CH (a)-Methyl piperidine (a) Prpecoline (119°) S G \(\frac{9}{6} \) 8600 by reducing (a) methyl pyridine in alcoholic so lution with sodium (Ladenburg a Roth, B 18, 47, A 247, 62, C R 103, 747) Colourless liquid, smelling like piperidine, v sol water, alcohol, and ether Separated by KOH from its aqueous solution Inactive, but if a crystal of hydrogen comme tartrate be added to a conc solution of the acid tartrate, crystals of the acid tartrate of dextrorotatory (a) methyl pyridine hexahydride separate, while the salt of the lævo rotatory isomeride remains as an oil The rota tion of the dextro (a) methyl piperidine is [a]n =21 44', while that of the lævo base is (pio bably) equal and opposite

Reactions -1Treatment with Br and NaOHAq yields (a) pipecolein $C_6H_{11}N$, an oily base (126°), S G $^{\circ}$ 880 (Ladenburg, B 20, 1645) Its acetyl derivative boils at about 230° -2 Combines with sulphide of carbon, forming methyl piperidine methyl piperyl di thio carb amate C.H.2N CS SC.H.4N, [119°], v e sol water and alcohol

Salts -B'HCl [189°] Colourless needles, sol water Not deliquescent —B'HBr [182°] Silky matted needles, m sol water — The platinochlorideisv sol water -The mercurichloride forms sparingly soluble plates

(β)-Methyl-pyridine C_sH₇N ι ε

N≪CH CH >CH m Picoline (β) Picoline (144° cor) SG 2 9771 (L), 9765 (B) Occurrence—In bone oil (Weidel, B

2008) and in coal tar (Mohler, B 21, 1009)

Formation -1 By distillation of acrolein-ammonia (Baeyer, A 155, 288, cf Claus, A.

Suppl 2, 134, 130, 185, 158, 222) -2 By heating CH,Br CHBr CH,Br with alcoholic ammonia at 250° (Baeyer) —8 By distilling strychnine with lime (Stochr, B 20, 2728, Löbisch a Malfatti, M 9, 632) -4 By heating acetamide (10 g) with glycerin (32 g) and \bar{P}_2O_s (26 g) (Zanoni, J 1882, 498, Hesekiel, B 18, 3091) — 5 Together with homologues, by distilling glycerin with (NH₄)₂SO₄ and a little H₂SO₄ (Storch, B 19, 2458) -6 One of the bases got by dis tilling brucine with lime (Behrend, J pr [2] 42, 415) -7 Together with tri methylene imine (66°-70°) by distilling tri-methylene diamine hydrochloride (Ladenburg a Sieber, B 23, 2729)

Purification -By digesting in hydrochloric acid solution with NaNO2 on a water bath, fol lowed by crystallisation of its mercury double

salt (Bachér, B 21, 293)

Properties -Liquid When prepared from strychnine it boils at 149°, and the base so obtained (called (B') methyl pyridine) is less soluble in water than the variety boiling at 144°, and forms a platinochloride melting at 258° in stead of 241° (Ladenburg, B 23, 2688) Optically inactive (Landolt, B 19 157) Less soluble in water than (a) picoline The absorption spectrum has been studied by Hartley (C J 41, 45) Oxidised by a 2 p c solution of KMnO₄ to pyridine

(β) carboxylic (nicotinic) acid Salts—B' H₂PtCl₆ aq Monoclinic prisms, v sol hot water Melts, when anhydrous, at 191° (L) or 195° (Stoehr) On heating at 120° for some time it gives off HCl, leaving B'zHPtCl, [214°] A boiling aqueous solution deposits B'PtCl, while B'2HPtCl, crystallises from the nltrate—B'HAuCl, [184°] Needles (from hot water), v sol alcohol -B'HHg,Cl, Needles (from water), plates or needles (from HClAq) or prisms (on slow crystallisation), v sl sol water, more sol HClAq -B', HgCl2 white $pp -B'.H_2ZnCl_4 \quad [158]$ Pearly needles, sol hot water - Picrate B'C, H2(NO2)3OH [145°] Needles or plates, m sol water and alcohol

(β) Methyl-pyridine hexahydride $C_6H_{13}N$ \imath ϵ NH CH CH CH2 CH, (B) Methyl piperidine (β) Picoline (B) Pipecolini hevahydrule $(125^{\circ})^{1}$ S G $\frac{9}{6}$ 8684 V D (H=1) 9814 Ob tained by reducing (8) picoline in alcoholic solu tion with sodium (Ladenburg, A 247, 67, Stochr, B 20, 2732, Hesekiel, B 18, 910) Colourless liquid, smelling like piperidine, v sol water When heated with MeI it forms C.H., NMe,I [192°] The hydrochloride of (B) methyl-pyr idine hexahydride is not ppd by HgCl

Salts —B'HCl Colourless needles, v e sol water and alcohol -B'HI [131°] Colourless, non deliquescent needles - B'H,PtCl, [192°] Orange yellow prisms, m sol water — B'HAuCl, [131°] M sol water — B'2H,CdI,aq White plates, melting at 145° when anhydrous B'2H4FeCy6 2aq yellow monoclinic prisms, less soluble than the ferrocyanides of homologous bases Decomposed by water at 75° -Picrate $B'C_6H_2(NO_2)_8OH$ [138°] Yellow pp, m sol

(γ) Methyl-pyridine C.H,N 2 6 NCH CH CH CMe p Picoline (γ) -Prooline. (148 5° cor) SG 9742

Occurrence -In coal tar, from which it may be obtained by preparing its platinochloride from the so-called lutidine (Schulze, B 20, 418, Ladenburg, B 21, 285, A 247, 11)

Formation—1 By heating di-chloro-pyr-

idine (γ) -carboxylic acid with conc HIAq and P at 175° (Behrmann a Hofmann, B 17, 2696) -2 In small quantity by heating pyridine methylo-rodide in sealed tubes at 300°, distilling the product with KOH, converting the fraction (142°-146°) into platinochloride, and decomposing the Pt salt by H2S (L) -3 By distilling

sparteine with lime (Ahrens, B 21, 828) Properties -Oil, smelling like (a)-methylpyridine, v sol water, alcohol, and ether Oxidised by dilute KMnO₄ to pyridine (γ) -carboxylic

(isonicotinic) acid [307°]

Salts —B₂H.PtCl₆ [231°] Fo plates, sl sol cold water —B'HAuCl₄ Four sided [2059 Prisms, v sl sol water -B'HHg₂Cl₃ [129°]. Needles, v sol hot, sl sol cold, water -P1. crate B'C, H2(NO2), OH [167°] Tufts of needles, sl sol cold water

(γ)-Methyl-pyridine dihydride C.H.N i e NH CH CH CH Formed from ethylpyrrole and HClAq at 130° (Dennstedt a Zimmermann, B 19, 2197) - B'2H PtCl4, red needles, v sol water

(γ) Methyl-pyridine hexahydride C,H, N ι e NH CH₂ CH₂ CHMe (γ) Pipecoline (126 5°-129° cor) SG 2 8674 Obtained by reducing (γ) methyl pyridine in alcoholic solution by sodium (Ladenburg, B 21, 288, A 247, 69) Colourless hygroscopic liquid which fumes in the air, and smells like piperidine V sol water

Salts -B'HCl v e sol water -B',H,PtCl, [203°] Prisms, m sol water — *B HAuCl. [1270] Yellow needles sl sol water *B',H.CdI, $[135^{\circ}]$ - Bismutho iodide characteristic red plates The picrate and mercury double chloride are crystalline

v Methyl-pyridine dihydride C,H,N $NMe < CH CH CH > CH_2 (?)$ (129°) Obtained by distilling pyridine methylo iodide with KOH (2 pts) and a little water (Hofmann, B 14, 1498) Very pungent oil, almost insol water Absorbs oxygen from the air Combines with bromine, with iodine and with sulphur Combines with CS and with mercaptan HClAq at 180° decomposes it, giving off methyl-

ν Methyl pyridine hexahydride C₆H₁₃N ι ε NMe CH₂ CH₂ CH₂ CH₂ Methyl piperidine. (105°) (L) Formed by adding potash to the product of spontaneous union of piperidine with MeI (Cahours, A Ch [3] 38, 76) Formed also by heating piperidine hydrochloride (10 g) with MeOH (75g) for 4 hours at 300°, excess of alcohol being distilled off, and the dry residue distilled with aqueous potash (Ladenburg, A 247, 56). Liquid —B'HCl Needles —B'2H2PtCl. Orange crystals, v sol water

Methylo-rodide B'MeI Crystalline, m sol hot alcohol When heated with solid KOH it yields oily 'di-methyl-piperidine' (1180), a strongly alkaline base, which is decomposed by gaseous HCl into methyl chloride and methylpiperidine 'Di methyl piperidine' forms the salts C,H,,NHCland C,H,,NHAuCl, It combines with halogens, forming crystalline C,H₁₅NI₂, C,H₁₅NICl (which yields C,H₁₅NIClAuCl₂), and C,H₁₅NBr₂. The latter is converted by moist Ag2O into crystalline C,H,1NBr, whence further treatment with moist Ag₂O produces C₇H₁₄NOH which is split up on distillation into H₂O and 'dı methyl piperideine' Ladenburg suggests the formula CH, CH CH CH CH NMe₂ for 'di methyl piperidine,' and Merling (B 19, 2628) suggests CH₂ CHBr CH₂ NMe₂Br for the com pound C,H,NBr, This dibromide is accom panied by an oily isomeride which may possibly be CH2Br CHBr CH2 CH2 CH2 NMe2, which changes into the other variety on heating its alcoholic The di nodide C, H15NI, is converted, on treatment with Ag O into 'di methyl piper ideine 'C,H13N, a liquid (137°-140°) which forms the salts $(C_7H_{13}N)$ H_2PtCl_8 and $(C_7H_{13}N)HAuCl_4$, and a methylo iodide $C_7H_{13}NMeI$ D1 methyl piperidine combines with MeI forming crystal line C₂H₁₈NMeI [200°] whence moist Ag O forms strongly alkaline C.H., NMeOH which is split up by heat into pirylene C,H, water, NMe,, MeOH, and di-methyl piperidine Di methyl piperidine also combines with methylene iodide forming C,H, NCH, I, (Ladenburg, B 14, 1347) Laden burg suggests for di methyl piperideine the CH CH

formula CH CH2 CH NMe

Methyl pyridine from Bone oil The follow ing salts described by Ramsay (P M Oct 1876 and 1877, July 1878) were prepared from a methyl pyridine obtained from Dippel's oil, which was probably (a) methyl pyridine mixed with a little (β) methyl pyridine — ×B'HCl [160°] White deliquescent crystals -B'HBr [187°] Deliquescent Absorbs bromine forming B'HBr, golden-yellow needles, sl sol water—
B'Br, Needles—*B'HI Decomposed by heat, yielding B'HI, which crystallises in brown needles [79*]—B ICl yellow tables—B'HgCl—B'HgCl—(at 100°) Converted by water at 170° into yellow flocculent B'2PtCl, and B'PtCl, a yellowish green insoluble powder -Platinocyanide B'2H2PtCy, 4aq yellow crystals The crude bone oil picoline forms the following com binations with alkyl salts —B'MeCl deliquescent needles (from alcohol) —(B'MeCl), PtCl, small cubes —B'MeI [227°] Long white deliques cent needles (from alcohol) —B'MeI, [129°] Bluish black feathery plates, insol water and CS₂, sol alcohol and ether —B'MeNO₃ trans parent prisms —(B'C₂H,Cl)₂PtCl₄ —B'₂C H₄Br₂
[276°] Small prisms The same picoline forms with acetyl chloride deliquescent brown crystals of B'AcCl According to Gardner (B 23, 1589) crude picoline forms with acetic and formic acids the salts (C₆H₇N)₂(HOAc)₃ (c 148°) and C₆H₇N(CO₂H_{2)₃} (156°-159°) which distil unchanged

Di methyl-di-pyridine (C₆H,N), Dipicoline Parapicoline (310°-320°) SG 112 HFp 8084 (Ramsay, that for picoline being 3755) Formed by boiling bone oil picoline (6 pts) with sodium (1 pt) for two days (Anderson, A 105, 344). Pale-yellow oil miscible with alcohol and ether. Bromine water gives a pp of

C₁₂H₁₂BrN₂H₂Br₂ —C₁₂H₁₄N₂H₂PtCl₆ pale yellow powder Its aurochloride is decomposed by bolling water (O de Connek, Bl. [2] 45, 131)

boiling water (O de Coninck, Bl [2] 45, 131) $Methylo \ vodude \ C_{i_1}H_{i_1}N_{i_2}(MeI)_{j_1}$ Yellow powder, v sol water, almost insol alcohol and ether Yields $C_{i_2}H_{i_4}N_{j_4}Me_{j_2}PtCl_{i_6}$ and $C_{i_1}H_{i_4}N_{j_4}Me_{j_5}I_{i_6}$

(αα) Di methyl pyridine C,H,N i e

N CMe CH CH (aa) Lutidine oo Lutidine Mol w 107 (142' cor) (L), 145° (E) SG § 942

Occurrence—In coal tar, being obtained by extracting with H SO₄, ppg by alkali, and separating from the isomeride (157°) by fractionating (Lunge a Rosenberg, B 20, 127, Ladenburg a Roth, A 247, 28) It occurs also in bone oil, and may be obtained from the fraction (135°-145°) (Roth, B 19, 786)

Formation —1 By the action of cinnamic aldehyde and alcoholic NH, on acetoacetic ether, the resulting dihydride of stylyl di methyl pyridine dicarboxylic ether being saponified, oxidised by KMnO₄, and the dimethyl pyridine thearboxylic acid so produced distilled with lime in a current of hydrogen (Epstein, A 231 18)—2 By distilling its dicarboxylic acid with lime (Engelmann, A 231, 54)—3 By distilling oxy dimethyl pyridine (lutidone) with zinc dust (Conrad a Epstein, B 20, 162)

Preparation—Clude picoline (139°-142) from bone oil is dissolved in excess of HClAq and a hot solution of HgCl is added Thidouble salt which is ppd is recrystallised and decomposed by aqueous NaOH. The base is finally separated by solid kOH (Ladenburg A 247, 30)

Properties—Liquid smelling and tasting like pyridine, sol cold water, the base separating again on warming. Its aqueous solution ppts solutions of ZnSO, CdSO, FeSO, and FeCl, With CuSO, it gives a pale blue ppnot turned black by heating. With AgNO, it gives minute needles of B AgNO, Dilute KMnO, oxidises it to pyridine dicarbovylic acid [2279]

Salts — *B'HCl Deliquescent needles — B'2H,PtCl₈ [208°] Orange red monoclinic plates, abc=892 1 660, \$\beta=81^\circ\$ 55' V sol hot, m sol cold, water, insol alcohol—B'HAuCl₄ [124°] Yellow needles (from very dilute HCl) —B'HHgCl₃ [186°] Thin plates (from acidulated water) —B'HHg,Cl₃ (Mohler, B 21, 1008) —B',H₂Cr₂O, [92°] Orange prisms —B'(NH₃)H,Ct O₇ [c 160°] —Picrate [159°] Yellow needles or thin plates

(aa) Di methyl pyridine hexahydride C,H₁,N ve NH CHMe CH₂ CH₂ (127°–130°) SG ⁹₀ 8492 Formed by reducing the corresponding di methyl pyridine in alcoholic solution with sodium (Ladenburg, A 247, 87 B 18, 54) Colourless liquid, miscible with water, alcohol, and ether -B'HCl non deliquescent needles, m sol water -B'HBr Needles, v sol water -B'2H₂PtCl₄ [212°].

orange red crystals
(a7) Dimethyl pyridine C,H,N r e

NCMe OH CMe. Lutidine (157°) S G

2 9493 S 20

Occurrence -In coal tar oil, being extracted with other bases by $H_3 \otimes O_4$ (Ladenburg a Roth, B 18, 913, Lunge a Rosenberg, B 20, 131), Ladenburg, 21, 286)

Formation -1 By distilling oxy di methyl pyridine CMe CH CO NH with zinc dust (Hantzsch, B 17, 2908) -2 By distilling its tri-carboxylic acid with lime (Hantzsch, A 215, 56) -3 By distilling with lime the acid N CMe C(CO₂H) CMe the ether of which is obtained by condensation of an equal number of molecules of acetoacetic ether, acetic aldehyde, and acetic aldehyde ammonia (Michael, B 18, 2020)

Preparation —The fraction of coal tar bases boiling between 155° and 160° is dissolved in dilute HClAq, conc HClAq is then added, fol lowed by a hot concentrated solution of HgCl, The double salt which then crystallises out is decomposed by distilling with NaOHAq (Laden

burg, A 247, 35)

Properties -Liquid, smelling like pyridine, dissolving in 5 pts of cold water, less soluble in hot water Miscible with alcohol and ether Oxidised by KMnO4 Easily volatile with steam to pyridine dicarboxylic (lutidinic) acid [235°] Reacts with benzoic aldehyde and ZnCl, forming styryl methyl pyridine (Bachér, B 21, 3071)

Salts -B'HHg Cl, laq aq Needles Melts at Mohler (B 21, 1008) 132° when anhydrous obtained from coal tar lutidine in acid solution a salt B'HHgCl, -B'2H PtCl, [220°] Plates or prisms -B HAuCl, amorphous pp, chan ging to prisms -*BHCl slender needles -*B'HBr Needles -Picrate [179°] Needles, sl sol cold water

 $(\alpha \gamma)$ D1-methyl-pyridine hexahydride

NH CHMe CH CHU (a₁) Di m thyl piper thine (141°) SG ² Soli Obtained b Obtained by reducing the corresponding di methyl pyridine in alcoholic solution with sodium (Ladenburg, A 217, 88) Colourless strongly alkaline liquid, smelling like piperidine Fumes with HCl sol water, v e sol alcohol and ether

Salts—B HCl [235°] I needles, v sol water—B'HBr Long colourless Br [142°] Short needles, v e sol water -B'H.PtCl, groups of

yellow needles

(ββ) Di-methyl-pyridine C H_oN s.e

N≪CH CMe CH (170°) S G 4 9614 Ob tained by heating with lime the di methyl pyridine curboxylic acid formed by oxidation of the (ββa) di methyl-ethyl pyridine produced by heating propionic aldehyde ammonia with propionic aldehyde (Durkopf a Göttsch, B 23, 1118) Transparent, strongly refracting liquid, with a pleasant odour characteristic of (β) alkyl pyridines, m sol cold water, sl sol hot water Yields on oxidation a pyridine dicarboxylic acid [815°]

Salts -B',H,PtCl [256°] Dark red needles and plates, sl sol water — B'HAuCl, [149°] Yellow needles, sl sol water — Mercury double chloride [176°] Long needles, al

sol cold water

(αβ')-Di-methyl-pyridine N<CH CH CH Vol. III

(162°-166°) Occurs in coal tar (Lunge a Ro senberg, B 20, 134) Yields isocinchomeronic (pyridine dicarboxylic) acid on oxidation

(av)-Di-methyl-pyridine tetrahydride?

C,H,,N 1.0 NMe CH CH CH, Formed, together with MeCl, hydrocarbons, methylamine, NH, and other bases, by heating anhydro ecgonine with conc HClAq (Einhorn, B 22, 1362) Oil When heated with conc HClAq at 280° it yields a mixture of bases which appear to yield methyl pyridine when distilled over zinc dust -B'HAuCl, [212°] Small needles, m sol water

-B'C, H₂(NO₂), OH Long needles, v ol sol hot water - *B'HCl very hygroscopic

Di-methyl-pyridine of bone oil (156°-159°) is a mixture of $(\alpha \gamma)$ di methyl pyridine, $(\alpha \beta')$ -di methyl-pyridine, (β) -ethyl pyridine, and (γ) -ethyl pyridine. The existence of these bases is shown by the production of the corresponding pyridine di and mono carboxylic acids on oxi dation by KMnO, (Weidel a Herzig, M 1, 1, Weidel a Pick, M 5, 658, cf Anderson, A 80, 5) Bone oil also contains (aa) di methyl pyr idine (v supra) Greville Williams (C J 7, 97, Pi 13, 311) obtained a lutidine from coal tar, this has since been shown to contain (aa), (ay), and (aB) di methyl pyridines (v supra) Oechs ner de Coninck (Bl [2] 41, 249) found (γ) ethyl pyridine (154°) in coal tar Lutidines have also been obtained by distilling the bituminous shale of Dorsetshire (Williams) and peat (Church a. Owen, P M [4] 20, 110) Among the products obtained by distilling cinchonine with KOH Occhener de Coninck (C R 91, 296) obtained a lutidine (165°), V D 3 8 (calc 37), S G 2 959, which formed a deliquescent crystalline hydro chloride and a platinochloride B'aHaPtCla crystal lising in orange red needles, converted by boiling water into B' PtCl, crystallising in yellow needles When brucine is distilled with KOH it yields a lutidine (166°) whence B'H.PtCl_a [180°] and B'.PtCl_a [205°] (Oechsner de Coninck, C. R. 95, 298, 96, 437). Lutidine aurochloride B'HAuCl_a is decomposed on boiling with water, yielding first thin red plates of B HAuCl, B', AuCl, and then a red crystalline pp B', AuCl, (O de Co ninck, Bl [2] 31, 634)

Di-methyl pyridine dihydride C H, N (199°) VD 33 Occurs in cod liver oil (Gautier a Mourgues, C R 107, 111, Bl [3] 2, 213) Co lourless strongly alkaline and caustic oil, absorbs CO, from the an Poisonous Its salts taste bitter Oxidised by boiling aqueous KMnO, to methyl pyridine carboxylic acid and a little pyridine carboxylic acid

Salts - *B'HCl confused needles, v sol water - *B'HNO, Reduces AgNO, - B'zH, SO, Groups of deliquescent needles -B'2H2PtCl Lozenge shaped plates, loses HCl on boiling with

Methylo rodide B'MeI Colourless needles, sol water and alcohol Yields a tri-methylpyridine dihydride on treatment with potash

Di-methyl-pyridine hexahydride Methylosodsde C, His NMeI [192°] Formed by heating (8) pyridine hexahydride with MeI and MeOH at 100° (Hesekiel, B 18, 3099, A 247, 69) Needles (from acetone) Not decomposed by aqueous KOH Yields (C,H₁₈NMeCl),PtCl₄, an orange crystalline pp turned black at 234° ВВ

(s) Tri-methyl-pyridine C.H., N : e N CMe CH CMe (γ)-Collidine (172° cor) (H, M); (168°) (D) SG 12 917 (H), 922 (M), z 9312 (D) Occurs in coal tar, from which it may be obtained by fractional distilla tion followed by ppn of the bases by K4FeCy6 (Mohler, B 21, 1011) Formed by heating with quicklime the potassium salt of its dicarboxylic acid, which is obtained by the action of nitrous acid on its dihydride produced from acetoacetic ether and aldehyde ammonia (Hantzsch, A 215, 32) Formed also by heating acctone with NH,Cl for 3 days at 265°, CH, being evolved (Riehm, A 238, 16), and by heating acctone with aldehyde ammonia for 10 hours at 200° (Dur kopf, B 21, 2713)

Properties -Liquid which turns brown in the More than 3 times as soluble in water as RIT aldehyde collidine Less soluble in hot than in cold water It differs also from aldehyde colli dine in giving a pp with AgNO3, an orange crystalline pp with CrO, and an aurochloride that melts under water It is oxidised by KMnO, to $N \leqslant_{C(CO_2H)}^{C(CH_3)} \stackrel{CH}{C} \searrow_{CMe}$ and uvitonic acid Bromine added to its solution in CS forms un stable orange crystals of C₈H₁₁NBr₂ (Pfeiffer, B

20, 1344)

Salts —B'HCl Slender, non deliquescent needles —B'₂H₂PtCl₈ yellow crystalline pp — B'HAuCl₄ [113°] (H), [115°] (M), [106°] (D) Needles (from hot water) —B'HHg Cl₈ [155°] — B'HI — *B'HNO, [above 300°] — B'₂H₂Cr₂O, Yellow prisms, decomposing at 190°—*B'₂H₂SO, [203°]—Pierate [156°] (M) Silky yellow needles, sl sol water, v sol alcohol

Reference -DI BROMO TRI MITHIL PYRIDINF Tri methyl pyridine dihydride CsH13N (175°-180°) Formed by hydro collidine heating its dicarboxylic ether (obtained from aldehyde ammonia and acetoacetic ether) with dilute HClAq at 130° (Hantzsch, A 215, 44) Pungent oil with alkaloidal smell Alkaline to litmus, v sol cold water Precipitates the hydroxides of Mg, Zn, and Fe from solutions of their salts -B' H2PtClc Minute needles which blacken at 200° -B'HI

Polymeride C₁₈H₂₅N₂ Tetrahydrodicollid-(255°-260°) Formed at the same time as the preceding — $C_{1e}H_{e}N_{e}H$ PtCl_e

s-Tri-methyl-pyridine hexahydride C_sH₁,N NH<CHMe CH2>CHMe Copellidine

(146°) SG z 8475 Formed by reducing tri methyl pyridine in alcoholic solution with sodium (Jaeckle, A 246, 43) Formed also, together with s tri methyl pyridine, by heating acetone with aldehyde ammonia at 200° (Durkopf, B 21, 2715) Liquid, smelling like piperidine, sl sol water, miscible with alcohol and ether Unlike s tri methyl-pyridine it gives a brownish-black pp with Hg2(NO3)2. Gives no pps with HgCl₂ or picric acid Salts—B'HCl Needles

Needles or prisms, v sol. water and alcohol -B'HBr -B'2H2PtCl

[205°] (J); [244°] (D)

Isomerides of tri methyl-pyridine v METHYL-ETHYL PYRIDINE, where (α) - and (β) collidines,

aldehyde-collidine and other isomerides are described

A collidine dihydride C, H, N, (210°), S G Q 1029, is contained in putrid horseflesh and putrid beef, and forms a crystalline hydro chloride and platinochloride (Gautier, Bl [2] 48, 12)

Tetra methyl pyridine dihydride C.H., N a.e NH < CMe CMe CMe CMeDihydroparvoline (159°) Formed by heating potassium pyriole carboxylate with MeI and McOH at 120° (Ciamician a Anderlini, B 21, 2862) Bas B'HAuCl₄ [110°] Yellow needles Basic liquid -

Tetra methyl pyridine hexahydride C.H., N NH CHMe CHMe CHMe Parpevoline (151°)Obtained by reducing the preceding in alcoholic solution with sodium (C a A) Liquid, smelling like pyridine Does not turn brown in air —B'HAuCl, [119°] Yellow needles

Methylo iodide B'MeI [262°] Prisms,

v sol water, insol ether

A parvoline C₉H₁,N (c 200°) is present among the products of the putic faction of horse flesh (Gautier, Bl [2] 48, 11) It is an oil which resinifies in the air, and forms a flesh coloured platinochloride

A parvoline C,H13N (188°) occurs among the bases obtained by distilling cinchonine with

KOH (O de Coninck, C R 91, 296)

Penta methyl pyridine dihydride C10H1 N ie NMe CMe CMe CMe (189°), (46° at

7 mm) Prepared by heating v methyl pyrrole with MeI, K2CO3, and methyl alcohol at 140° (Ciamician a Anderlini, Rend Accad Line [4] 203, B 21, 2863, 22, 658) Formed also by heating tetra methyl pyridine dihydride with MeI (Anderlini, B 22, 2507) alkaline reaction—B'HAuCl, Oil, with strong [100°] Yellow needles Reacts energetically with MeI, form ing an oily product, whence successive to it ment with AgCl and AuCl, yields C, H, NHAuCl, which crystallises in thin golden yellow needles

METHYL PYRIDINE CARBOXYLIC ACID

 $C_7H_7NO_2$ se $N < CH CH CH CO_2H$ carborylic acid Formed by heating methyl pyridine dicarboxylic (uvitonic) acid at 275° (Bottinger, B 14, 67, 17, 92) Filmetric crys tals (containing aq), sol hot, sl sol cold, water and alcohol, nearly insol ether Sublimes without melting Forms salts both with acids and bases Yields on oxidation with KMnO, pyridine dicarboxylic (lutidinic) acid

prisms - BaA'211aq Salts -HA'HCl very soluble needles - CaA aq very soluble four sided colourless prisms -CuA'2 aq blue pp - *AgA' white pp

Methyl-pyridine carboxylic acid C,H,NO, te N CH CH CH CMe. Homonicotinic acid [212°] Methyl-carbopyridic acid Obtained by heating methyl pyridine dicarboxylic (methyl-quinolinic) acid at 170°, or by warming it with HOAc (Hoogewerff a Van Dorp, R T C 2, 21) Formed also by the slow oxidation of (β) colhdine by KMnO, (O de Comnek, A Ch [5] 27, 493, Bl [2] 43, 107) Needles, v sol hot

water Oxidised by KMnO4 to pyridine dicarboxylic (cinchomeronic) acid

Salts -KA' small plates -CuA' blue crystals -AgA' needles -HA'HCl small prisms — (HA')2H2PtCl6 orange prisms HA'HAuCl, yellow needles

(a)-Methyl pyridine (β) carboxylic acid C,H,NO, 10 NCH [207°] сн с ∠со,н

Formed by oxidising (a) methyl (b') ethyl pyridine (aldehyde collidine) with a 2 pc solution of KMnO4, allowing the mixture to stand for 48 hours, and then heating to 60°. The filtrate from MnO, is neutralised by H,SO, and evapo nated, the residue is extracted with alcohol and the acid purified by means of its silver salt (Durkopf, B 18, 3432, Ladenburg, A 247, 43) Prisms, v e sol water and alcohol On distil lation with lime it yields (a) methyl pyridine (128) h MnO, oxidises it to pyridine dicarboxylic (isocinchomeronic) acid

Salts — (HA') H, PtCl, [240°] Aggregates of needles, v sol water, insol ether alcohol (CuA'2) Cu(OAc)2 Crystalline powder, formed by boiling a solution of the acid with cupie The silver salt is amorphous aurochloride forms yellow needles [c 202°]

Methyl pyridine carboxylic acid C H NO 1e N ≪ C(CO₂H) CH CH CH (?) [c 260°] Formed in small quantity, together with pyridine (αγ)di carboxylic acid, by oxidising $(\alpha \gamma)$ di methylpyridine with KMnO₄ (Bicher, B 21, 3000) Plates (from alcohol), v e sol water It is possibly identical with the isomeride described by Bottinger (v supra)

(β) Methyl-pyridine (β) carboxylic acid N CH CMe CH CCO H) [216°] Formed by

heating (B) methyl pyridine (aB') dicarboxylic acid with HOAc and Ac O at 2250 (Durkopf a trottsch, B 23, 1113) White mass, m sol Its aqueous solution is not coloured by water FeSO,

Methyl pyridine dicarboxylic acid

 $C_{s}H_{s}NO_{s}\text{ a.s. }N\leqslant\underset{C(\mathrm{CO\ H})}{C\mathrm{He}}CH>\!\!\!>\!\!C\ \mathrm{CO}_{s}H$ tonic acid [274°] Formed by the action of ammonia on pyruvic acid (Bottinger, A 188, 330, 208, 138, B 13, 2032, 16, 35, 17, 144) Formed also by oxidising s tri methyl pyridine, or di methyl ethyl pyridine, N CMc CH CLt, with KMnO, (Altar, A 237, 191, Dukopf, B 21, 2717) Minute six sided trimetric plates (Fried lander, J 1882 367), v sl sol cold, sl sol hot, water, m sol NH, Aq and HClAq v sol aniline, phenol, HOAc, and glycerin, sl sol isoamyl alco hol and chloroform, insol benzene and CS, Gives a violet red colour with FeSO, It is a powerful antiseptic Yields (a) methyl pyridine on distil lation with lime Split up by heat into CO. and NeCH CH OCO.H Alkaline KMnO. oxidises it to pyridine tricarboxylic acid Brom me water forms bromoform, CO, and formic scid

powder -- CaA" 6aq: Salts -(NH.)HA". amorphous -CaA" 4aq:

slender needles — CuA'' 4aq — $Cu_1(OH)_2A_2''$ 9aq *PbA" dense pp —Ag₂A" aq gelatinous pp Methyl pyridine di carboxylic seid

 $N \leqslant_{CH}^{C(CO_2H)} \xrightarrow{C(CO_2H)} CM^{44}$ C,H,NO, Methyl quinolinic acid [c 183°] 8 84 at 10°. Formed by the oxidation of (Py 1) methylquinoline (lepidine) (1 pt) by KMnO₄ (7½ pts) (Königs, B 12, 983, 14, 103, Hoogewerff a. Van Dorp, R T C 2, 15, B 13, 1639, 14, 645) Tables or prisms, sol hot, sl sol cold, water, sl sole alcohol, ether, and benzene Decomposes on fusion into CO and methyl pyridine carboxylic acid [210°], which on further oxidation vields cinchomeronic acid KMnO₄ oxidises it to pyridine (a) tricarboxylic acid The aqueous solution of the acid gives pps with the acctates of Pb, Ba, and Cu, and a yellow colour with

Salts -KHA" 2aq needles -KHA" 3aq -

Ag, A"aq erystalline powder

1 cSO.

Methyl pyridine dicarboxylic acid CaH, NO. ee N CHe C(CO,H) CH Methyl directing acid [245°-250°] I ormed from methyl pyridine tricarboxylic acid N C (CO H) C (CO H) CH by heating at 150° (Weber, 4 241,9) Spherical groups of needles (containing aq), al sol cold water KMnO, oxidises it to a pyridine tricub oxylic acid -HA'HClaq transpirent efforescent crystals —PbA" 2aq crystalline pp
Methyl pyridine dicarboxylic acid

N < CH - CMe > CH or N < C(CO,H) CMC > CH

Obtained by oxidising the di methyl ethyl pyridme, which is formed by the action of NH, on propionic aldchide (Durkopf a Gottsch, B 23, 685, 1110), and by the action of parallehyde on propionic aldchyde a minonia (Durkopf a Schlau k, B 21, 834). White powder (from hot The K, Ag, and Cu salts are sl sol. water

[127] Cincholouponic acid A product of the oxidation of cinchonine by chromic acid mix ture (Skiaup, M 9, 786) Prisms (containing aq), v e sol water, insol alcohol and ether Ac.O at 125° forms an amorphous acetyl derivative C₂H₁₂AcNO₄ Distillation of the lead salt over zinc dust yields a small quantity of pyridine Salts —PbA" powder, v e sol water

powder, v e sol water-H A"HCl [194°] Trimetrio crystals [a]_b = 31 4° at 18 7°

Nitrosamine C.H,2(NO)NO, [163°] Trimetric crystals, sl sol cold water, m. sol alcohol Warm cone HClAq reproduces C,H13NO, and nitrous acid -BaA" (at 115°) Deliquescent amorphous powder, in sol alcohol

In the preparation of cincholeuponic acid a base called cincholeupone C₂H₁₇NO₂ 18 also formed It yields cincholeuponic acid on oxidation with chromic acid mixture, and ethylpyridine on distillation over red hot zinc-dust. It forms the salts (C.H., NO.) HCl [200°], prisms —BaA" 2aq: B'H.PtCl. Staq and B'HAuCl. [203°], an acetyl derivative C.H. AcNO. [121°], and a nitrosamine

C,H, (NO)NO, [84°]
Methyl-pyridine tricarboxylic soid C,H,NO, s.s. N CMe C(CO,H) C(CO,H) CH [226°] Formed

by oxidising $N \leqslant_{CMe}^{OMe} \stackrel{C(CO,H)}{C(CO_2H)} \gg_{CH} \text{ with } KMnO_4$ (Weber, A 241, 6) Spherical aggregates (containing aq) At 150° it slowly gives off CO₂, yielding methyl pyridine dicarboxylic acid [245°-250°] —KH,A''', 6aq spherical aggregates —AgH,A'" 2aq needles (from hot water)

Methyl-pyridine tricarboxylic acid

Methyl carbo-Formed by the oxidation of dinicotinic acid (ay)-di-methyl pyridine dicarboxylic acid by KMnO₄ (Weber, A 241, 25) Needles (containing aq) or prisms (containing 2aq) Less soluble in water than the preceding acid Turns yellow at 205°, and completely decomposes at 260° FeSO, colours its solutions deep red The cal-FeSO₄ colours its solutions deep red cium salt yields (γ) methyl pyridine on distilla-

Methyl-pyridine tricarboxylic acid

N < C(CO₂H) C(CO₂H) > CMe Picoline tricarb-Formed by the oxidation [238°] oxylic acid of flavenol (1 mol) with KMnO, (9 mols) (Fischer a Tauber, B 17, 2926) Formed also by oxidising potassium tri methyl pyridine carboxylate with aqueous KMnO, (Michael, A 225, 140) Slender needles (from water) Does not com-On further oxidation with bine with acids KMnO₄ it yields pyridine tetra carboxylic acid [227°] FeSO₄ colours its solution brownish-red

Salts -BaA" amorphous pp -Ag2A" Methyl-pyridine tetracarboxylic acid

 $N \leqslant_{C(CO_2H)}^{C(CO_2H)} \stackrel{C(CO_2H)}{C(CO_2H)} \geqslant_{CMe}$ C, H, NO, [199°] Obtained by boiling potassium trimethyl-pyridine dicarboxylate with a solution of KMnO, (Hantzsch, A 215, 57) Small prisms (from water), v e sol water, m sol alcohol, sl sol ether Gives (γ) picoline on distillation with lime Its neutral salts crystallise with difficulty Neutral solutions give pps with salts of Pb and Ag, mercurous salts, and Ba(OAc)2, but no pps with dilute BaCl, or with salts of Mg, Zn, Mn, Ni, Co, and Cu, and mercuric salts -K2H2A1v4aq large trimetric tables, v sol hot water, with acid reaction —KH₃A^{iv}2aq —Ca₂A^{iv}4aq, ppd by adding NH₂ and CaCl₂ —Mg₂A^{iv}6aq

D1-methyl-pyridine carboxylic acid

C.H.NO. 1 e N CH CH CH CH Lutidine Obtained by saponifying with carboxylic acid alcoholic potash its ether, which is formed by adding acetic aldehyde (50 pts) to a mixture of aceto acetic ether (130 pts) and aldehydeammonia (61 pts), the reaction, which sets in at once, being completed by heating to 100° (Michael, B 18, 2020) Transparent prisms (containing 2 aq), v sol water and alcohol Gives (a7)-lutidine on distillation with lime On exidation with KMnO, it yields pyridine dicarb-

oxylic (carboninchomeronic) acid Salts.—HA'HCl [166°] Large prisms or thick tables — (HA')₂H₂PtCl₄2aq [216°].

Reddish-yellow prisms Ethyl ether EtA' (246° uncor) Yellowish

oil, not volatile with steam — (EtA), H, PtCl [191°] Thin yellow pointed prisms, v. sl sol. water and strong alcohol

D1-methyl-pyridine carboxylic acid

 $N < CMe \longrightarrow CH \longrightarrow CMe$ Di - methyl - picolinieacid [153°] Formed by oxidising s-tri-methylpyridine with KMnO, (Altar, A 237, 183) Small crystals, v e sol water and alcohol, m sol ether Yields (αγ) di methyl pyridine on distillation with lime Its metallic salts are v sol water —B'HCl aq minute white needles, ▼ e sol water — B'2H2PtCl4EtOH Prisms

D1-methyl pyridine carboxylic acid

 $N < \begin{array}{c} \text{CMe} & \text{CH} \\ \text{CMe} & \text{C(CO}_2\text{H}) \\ \end{array} > \text{CH} \quad \textit{Dr-methyl-nucotinue} \\ \textit{acid} \quad [160^\circ] \quad \text{Prepared} \quad \text{by distilling the mono} \\ \end{array}$ Dr - methyl - nicotinic ethylic ether of di methyl pyridine dicarboxylic acid N CMe C(CO,H) CH (Weiss, B 19,1308) Needles (containing | aq), v e sol water Oxidised by KMnO, to the corresponding pyr idine tricarboxylic acid —AgA' - HA HCl small prisms — (HA'), H. PtCl, 2aq orange needles
Di-methyl-pyridine carboxylic acid

 $N < CH \longrightarrow CMe \longrightarrow CH$ [1510] Formed by oxidising the parvoline obtained from propionic aldehyde and NH, (Durkopf a Göttsch, B 23, 687, 1110) — (HA')₂H₂PtCl₆EtOH V sol water,

sl sol alcohol Decomposes at 260°

Di-methyl-pyridine carboxylic acid C₂H₂Me₂N CO₂H Formed by saponifying, by alcoholic potash, its ethyl ether, which is produced from acetoacetic ether (30 g) by heating with formic aldehyde (5 g) and ZnCl, (30 g) for 12 hours at 100° (Canzoneri a Spica, G 14,449) Silky needles, v e sol water – HA'HClaq [220°] Transparent rhombohedra (from ter) — (HA')₂H₂PtCl_s red crysta's Ethyl ether EtA' (260') Oil water) -

Di-methyl-pyridine dicarboxylic acid

 $C_0H_0NO_4$ so $N \ll_{CH}^{CMe} \frac{C(CO_2H)}{C(CO_2H)} \gg_{CMe} (\alpha\gamma) D\iota$ methyl-di nicotinic acid` [258°] Obtained by heating (ay) di methyl pyridine tricarboxylic acid at 175° (Weber, A 241, 20) Formed also by oxidation of the corresponding tetra methyl pyridine (Durkopf a Gottsch, B 23, 1112) Needles (containing 2 aq (W) or anhydrous (D aG) PbA" Its solution is not coloured by FeSO. PbA" gelatinous pp, becoming crystalline on boiling —H₂A"HCl aq slender needles, decom posed by water —(H₂A")₂H₂PtCl_e orange tables, melting above 300°

D: methyl pyridine dicarboxylic acid $N \leqslant \frac{CMe}{C(CO_2H)} \frac{CH}{C(CO_2H)} \searrow CMe$ or N < C(CO, H) CH > CMe[245°].

Formed by oxidising s tri methyl pyridine carboxylic acid in neutral solution with KMnO. (Michael, A 225, 137). Prisms (from water).-CaA" -MgA" Saq -(H,A"HCl),PtCl, 6aq Di-methyl-pyridine dicarboxylic acid

N CMe C(CO₂H) OH Lutidine dicarboxylic acid Formed by saponifying with alcoholic potash its ether, which is produced by passing nitrous acid gas into di methyl isopropyl dicarboxylic ether in alcohol (Engelmann, A 231, 50) Its ether is also one of the products of the action of acetoacetic ether on hexamethylene tetramine at 170° (Griess, B 21, 2740) The same ether at 170° (Griess, B 21, 2740) appears to be formed by oxidising with nitrous acid gas the product obtained by the action of phenyl acetic aldehyde on aceto acetic ether and ammonia (Jeaurenaud, B 21, 1784) Slender needles (containing ‡ aq) Melts at a very high temperature V al sol cold water, alcohol, and ether KMnO oxidises it to pyridine tetracarboxylic acid On distillation it yields CO, and di-methyl pyridine carboxylic acid Distillation over CaO yields (aa) di methyl pyridine

Salts —BaA" 2 aq —PbA" 2aq amorphous pp changing to stout prisms —H₂A"HCl 2aq prisms

Mono ethyl ether EtHA" [181°] tained by decomposing the di ethyl ether (1 mol) with alcoholic KOH (1 mol) (Weiss, B 19, 1308) Needles (from water) Its neutral solu tion is ppd by salts of Ag, Hg, and Cu — EtHA"HCl 2aq [90°] Needles (from water)

Diethyl ether Et,A" [72°] (302°) Long white needles — Et.A"HAuCl, ve sol alcohol

Di methyl pyridine dicarboxylic ether di

hydride C,H,NMe2(CO2Et), [170°] by heating acctoacetic ether (20 g) with ZnCl. (20g) and hexamethylene tetramine (4g) at (Griess & Harrow, B 21, 2740) sided plates or needles, almost insol water, sl sol cold alcohol and ether, v sol chloroform By treatment with nitrous acid, or even by solution in hot dilute HCl, it is oxidised to C,HNMe,(CO,Et)..

Di methyl pyridine tricarboxylic acid

 $C_{10}H_9NO_e$ to $N < CVe_{C(CO,H)} C(CO,H) > CMe$ tedine tricarboxylic acid Dimethylcarbodini

cotinic acid [2120] Formed by oxidation of potassium tri methyl pyridine dicarboxylate with KMnO₄ in a solution kept neutral by CO₂ (Hantzsch, A 215, 52, Weber, A 241, 20) Crystallises from water in hard crusts composed of rhombohedia (containing 2aq) Split up by heat into CO, and (ay)-di-methyl pyridine di carboxylic acid Yields (ay) di methyl pyridine on distillation with lime Its neutral solutions give no pps with salts of Cu, Ag, or Pb, nor with FeCl, but with Hg(NO,), a pp soluble in hot water

- KH₂A''' 2aq Salts -- Ba,A'',8(?) aq minute needles -Mg,A", 10aq -Ca,A", 8aq

Di methyl pyridine tricarboxylic acid

 $N \leqslant_{CMe}^{CMe} \frac{C(CO_2H)}{C(CO_2H)} \geqslant CCO_2H$ 178 at 8° Formed by oxidising potassium styryl di methylpyridine dicarboxy late with cold aqueous KMnO, (Epstein, A 231, 11) Crystallises from water in pri-ms (containing aq), almost insol water, alcohol, ether, benzene, and chloroform Turns brown at about 220° but decomposes without melting Gives (aa)-di methyl pyridine on distillation with lime A solution of its ammonium salt gives pps with CaCl., CdSO., Hg₂(NO.),, AgNO., SnCl., Pb(OAc)., and Bi(NO.), but not with BaCl., MgSO., MnSO., and alum, nor, in the cold, with ZnSO, or CuSO, FeCl, gives a reddish colour

Salts.-H.A"HCl needles, decomposed by

and by water alcohol - Ph.A", 6aq. -Cu(NH₄)A" 4aq —Ag₂A" 3aq

Tri-methyl pyridine carboxylic acid

C₀H₁₁NO₂ to N CMe C(CO₂H) CMe. Colledine [155°] Obtained by saponi carboxylic acid fying with alcoholic potash its ethyl ether, which is obtained by passing nitrous acid into its di-hydride (Hantzsch, A 215, 42) and by heating the mono-ethyl ether of tri methyl pyridine dicarboxylic acid (Michael, A 225, 131) Crystallises from water in short needles or cubes (containing 2aq) Melts at 110° when hydrated, or 155° when anhydrous On oxidation with KMnO, it yields di methyl pyridine dicarboxylic

acid, methyl pyridine tricarboxylic acid, and pyridine tetracarboxylic acid Salts — KA' n CaA', aq — HA'HCl (HA'), H, PtCl, aq needles (from alcohol) needles or prisms. --

Ethylether EtA' (256°) S G 15 1 0815 Liquid, v sol ether, alcohol, benzene, and chloroform, insol water, sol dilute acids—
(EtA')₂H₂PtCl₆ [193°] Prisms (from alcohol)
—EtA'MeI [128°] Needles, v sol water and alcohol, msol ether With Ag₂O it yields crys talline C10H12NO2 3aq, whence C10H12NO2HCl aq (Hantzsch, B 19, 35)

Tri methyl pyridine dihydride carboxylic ether C,H,NMe, CO,Et Formed by warming C.H.NMe,(CO,Lt), with HClAq (of 25 pc) at 100° (Hantzsch, A 215, 40) Feebly basic oil.—

(HA)₂H₂PtCl₆ minute needles
Tri methyl pyridine dicarboxylic acid $C_{10}H_{11}NO_4$ so $N \leqslant_{\hbox{CMe }C(CO,H)}^{\hbox{CMe }C(CO,H)} \geqslant_{\hbox{CMe.}}$

Formed by saponifying with alcoholic potash its ether, which is obtained by the action of nitrous acid gas and alcohol upon its dihydride, which is itself produced by the action of aldehydeammonia on aceto acetic ether (Hantzsch, A. 215, 26) Fluffy mass of needles (from hot water), melting above 300°, v sl sol cold, v sol hot, water, v sl sol alcohol and ether Oxidised by KMnO, to di methyl pyridine tri carboxylic acid, methyl pyridine tetra carboxylic acid, and pyridine pentacarboxylic acid Decomposed by heat into CO₂ and tri methyl pyridine carboxylic acid Bromine acting on an aqueous solution of the K salt yields di bromos tri methyl pyridine The salts which it forms with alkalis and alkaline earths are very solu ble, crystallise badly, have an alkaline reaction, and split up on heating into s tri-methyl-pyr idine and carbonates FeCl, gives an intense red colour to a solution of the K salt.—K,A"— CaA"aq needles — BaA"3aq — MgA"3aq — (CuA"),CuO 11aq — Ag,A" — H,A"HCl 2aq — (H,A"),FH,PtCl,

Di-methyl ether Me,A" [82°] Formed by oxidation of its dihydride by nitrous acid (Hantzsch, B 16, 1947) White needles, v sol water -Me.A"HCl 2aq long glistening prisms melting, when anhydrous, at 142°me,A*),H,PtCl, [200" [200°] Örange spangles.— [105°] Slender light yellow needles. — * Me, A"HNO, [140°] Prisms

Mono ethyl ether EtHA" 2aq Formed from the neutral ether by boiling with the calculated quantity of potash dissolved in alcohol. Needles in radial groups (from alcohol), v. sol. water, v. sl sol ether Melts, when anhydrous, at 157° — HEtA"HCl [178°] Gubes — (EtHA"),1\perp PtCl,2\text{aq} prisms (from cold water) Welts, when anhydrous, at 219° —BaEt,\(\Lambda\)', 3\text{aq} — BaEt,\(\Lambda\)', 3\text{aq} — cdet,\(\Lambda\)', 2\text{aq} — needles — GuEt,\(\Lambda\)', 2\text{aq} — monoclinic prisms

\[D_1\cdot ethy \(\text{i} \) ether Et,\(\Lambda\)' (308°-310°)

\[S G \] 1087 Formed from its dihydride

Di-ethyl ether Et₂A" (308°-310°)

BG 18 1087 Formed from its dihydride (v infra) by treatment with HNO, or, better, by alcohol and nitious acid gas (Hantzsch, A 215, 21) Bright yellow viscid oil with faint odour and burning taste Not volatile with steam It has no action on litmus It does not ppt metallic salts With HgCl₂ it gives, only after a time, silky needles of a double compound it dissolves in dilute acids—Et₂A"HCl very hygroscopic—(Et₂A")₂H₂PtCl₆ rose-coloured tables [184°]—Lt₂A"HNO₃ needles [92°] Et₂A"HI [170°-173°] Dark plates, which issolve with rotation in cold water—Et₂A"HI,

violet pyramids

Methylo rodide of the diethyl ether Et. A'Mel [140°] Formed by heating the ether with Mel and MeOH at 120° Crystalline mass, more soluble in water or alcohol than Et.A"HI It is ppd unaltered from its aqueous solution by NaOH Its aqueous solution is acid to litmus It is not affected by fuming HCl at 150° or by alcoholic NH, at 150° Concentrated aqueous KOH forms methyl di carbocollidylium dehydride C,1H,3NO, substance crystallises in needles, [92°], v e sol alcohol, v sl sol cold water, and distils without decomposition at a temperature far above 360° It has neither acid nor basic properties When heated with H2SO, at 150°-180° it yields CO, HOAc, and methyl pseudo lutidostyril $C_8H_{11}NO$ When methyl dicarbo collidylium dehydride ' is heated in a current of HCl it loses CO_2 and forms methyl-carbo collidylum dehydride $C_{10}H_{13}NO_2$. This is also an indifferent body, it crystallises in needles [103°], v sol water, and boils above 340° On heating with H₂SO₄ it evolves acetic acid and gives methyl pseudo lutidostyril (Hantzsch, B 17, 1022)

Methylo-chloride of the diethyl ether Et,A"MeCl Formed by treating Et,A'MeI with AgOl (Hantzsch, B 17, 1019) Crystals Yields (Et,A"),Me,PtCl, which crystallises in thick

yellow prisms

Tri methyl-pyridine dihydride dicarboxylic acid C₁₀H₁₂NO₄ te NH CMe C(CO H) CHMe Methyl ether Me₂A" [156⁵] Formed

Methyl ether Me,A" [156°] Formed by the action of methyl acetoacetate on alde hyde ammonia (Hantzsch, B 16, 1946) When heated with HCl it exchanges CO,Me for H and yields the methyl ether of the monocarboxylic acid On oxidation with nitrous acid it gives C,Me,(CO,Me),N

Di-ethyl ether Et₂A" [131°] Formed by heating aceto acetic ether (52 g) with alde hyde ammonia (13 5 g) (Hantzsch, A 215, 8)

Properties —Compact colourless tables with many facets (from alcohol), with bright-blue fluorescence V sl sol boiling water, sl sol cold alcohol, ether and CS₂, m sol benzene, v sol boiling alcohol, v e sol chloroform. Boils above 315° with decomposition

Reactions -1 Boiling cone KOHAq has no action -2 Alcoholic NH, at 150° has no action 8 Alcoholic potash slowly decomposes it, form ing NH, and K2CO30-4 Boiling dilute acids do not dissolve it, it forms no platinochloride -5 Cone H.SO, dissolves it, but on pouring into water it is reppd unchanged —6 Warm cone HCl completely destroys it, forming CO2, EtCl, NH, aldehyde, and acetone -7 HCl passed into an ethereal solution removes the H2 (Hantzsch, A 215, 87), and forms other products — 8 Aqueous HCl (25 pc) at 100° forms hydro tri methyl pyridine mono carb oxylic ether —9 Dilute HCl at 130° forms ethyl chloride, CO, and tri methyl pyridine dihydride Another product is an oil composed of a ketone $C_oH_{1,0}$ (208°-209°), \forall D 4 20, which combines with NaHSO₃, and with bromine, and with hydroxylamine yields crystals [76°] -10 N_{ν} trous acid removes H2, leaving tri methyl pyr idine dicarboxylic ether -11 Bromine dissolved in CS₂ forms a dibromide of di bromo tri methyl pyridine dihydride carboxylio ether NC₈H,Br₂(CO₂Et)₂H,Br₂[88°] This is extremely soluble in boiling alcohol, and crystallises as yellow twin crystals Fuming HNO, converts it into the di bromide of di bromo tri methyl pyridine di carboxylic ether [102°] -- 12 Chloride forms the di chloride of penta chloro tri methyl pyridine dicarboxylic ether, crystallising as woolly needles [150°]

Tetra methyl pyridine dihydride carboxylic

ether $C_{15}H_{23}NO_4$ i e

NMe CMe C(CO,Et) OHMe [86°] Formed

by the action of paraldehyde and H₂SO₄ on methyl amido oxy butyric ether (Kuckeit, B 18, 620), and, in small quantity, by the action of methylamine on a mixture of acetoacetic ether and aldehyde (Hantzsch, B 18, 2580) Crystals, with blue fluorescence

METHYL-PYRIDINE-HYDRIDES v METHYL
PYRIDINE

DI - METHYL - DIPYRIDYL C_{1,2}H₁₂N₂ * 6 NC,H₃Me C₂H₃MeN Dipicolyl [84°] (295°–298°) Obtained by treating (a) picoline with sodium at 80°–90°, exposing the product to air, and fractionally distilling (Ahrens, B 21, 2930, Heuser, J pr [2] 42, 430) Very deliquescent yellowish needles With water it forms a compound (containing 4aq) melting at 38° When oxidised by potassium permanganate it yields NC₃H₃Me C₃H₃N CO₂H [193°], which on heating by itself or with HOAc yields methyl dipyridyl [94°]—B"H₂Cl₂ Hygroscopic plates (from al cohol) Picrate B"2C₃H₂(NO₂),OH [240°]—B"H₂Cl₂GH₂Cl₂ [220°]—B"H₂PCl₂ small plates, v sl sol water, v sol HClAq Discolours at 235°, but only partially decomposed at 275°—B"2HAuCl₄ nodules (from cone HClAq) decomposes at 200° (A), [210°] (H)—The tin double sait melts at 180°

Di methyl-dipyridyl dodecahydride $C_{12}H_{24}N_{3}$ to MeNC,H, $O_{2}H_{3}NMe$ Di-methyl dippyridyl. (230°-235°) Formed, together with tri methyl dipyridyl dodecahydride, by treating the product of the action of MeI upon dipyridyl dodecahydride (dipperidyl) with Ag₂O (Liebrecht, B. 19, 2595) Liquid, miscible with water, but separating on addition of NaOH—B'H₂Cl₂(HgOl₂)₃:

docculent pp, sol hot water -B"H2PtCla small water, v sol chloroform Its molecular weight

dark red crystals

Tri-methyl dipyridyl dodecahydride $C_{12}H_{26}N_2$ Formed as above Yellowish oil, insol water $(205^{\circ} - 212^{\circ})$ yellowish red crystals, v e sol water

TRI METHYL-PYRIDYLENE DIHYDRIDE DIKETONE DI-METHYL C₁₂H₁₇NO, $N \! \ll_{\mathrm{CM\,e~CH(CO~CH')}}^{\mathrm{CH\,Me~C(CO~CH')}} \! \! \! >_{\mathrm{CM\,e}}$ [153°] in vacuo) Formed by heating methylene dimethyl diketone (2 mols) with aldehydeammonia (1 mol) on the water bath (Combes, Bi [2] 51, 15) Hexagonal prisms (from alcohol), insol water

METHYL PYRIDYL ACETYLENE TETRA-HYDRIDE C.H NNe C CH Formed by boiling the hydrobromide of anhydro ecgonine dibromide with aqueous K2CO, (Eichengrun a Einhorn, B 23, 2879) Oil -B'H AuCl. [179°

DI METHYL DI PYRIDYL PROPANE DO

DECAHYDRIDE C1,H10N2 1 e

(C H, NMe CH), CH2 Methylo rodide B"Me I Obtained by heating (C H, N CH2), CH2, with MeI (Ladenburg, B 21, 3102) White non hygroscopic crystals, v sol hot water The aurochloride B"(HAuCl,) [171°] obtained from the methylo iodide, crystallises from water in needles

 $(Py \ 15)$ DI METHYL PYRIDYL- $(Py \ 3)$ -QUINOLINE C, H,

СН СН C,NH,Me, C,H, Lutidyl quinoline

[109°] Colourless glistening crystals Formed by heating m amido phenyl di methyl pyridine C, NH (CH3) C, H, NH with glycerine, nitrobenzene, and H SO, The chloride and nitrate form white needles, the platino chloride small orange needles, the auro chloride, long golden yellow needles '215°] (Lepetit, B 20, 2399, G 17, 473)

METHYL - PYROCATECHIN C H₈O₂ 1 e Formed by heating C₆H₃Me(OH) [134 creosol C.H. Mc(OMc)(OH) [131] with HIAQ (H Muller, C N 10, 209) Formed also by the dry distillation of dioxy toluic ((a) homo protocatechnic) acid (Tiemann a Nagai, B 10, 210) and from C,H,Me(NO)(OH) [1 3 4] by dis placement of NO by OH (Nevile a Winther, B 15, 2983) Liquid, which may be distilled, v e sol water, alcohol, and ether Reduces Fehling's solution and ammoniacal AgNO, in the cold FeCl, gives a green colouration, turned reddishviolet by ammonia

Mono methyl ether C.H.Me(OH)(OMe) [134] Isocresol (c 185°) Prepared from C_eH,Me(NH₂)(OMe) [134] by the diazo reaction (Lumpach, R 22, 250) (Limpach, B 22, 350) Yellow liquid, v sol alcohol and ether, al sol water Volatile with

Mono methyl ether C.H.Me(OMe)(OH)

[1 3 4] v CREOSOL

Isomerides v Methyl ethers of Pyrocatechin TETRA-METHYL PYROCOLL C14H14N2O2 26 $NO_4HMe_2 < CO > C_4HMe_2N$ [272 5°]

together with $(\alpha \beta')$ -di methyl pyrrole, by heating (αβ') di-methyl pyrrole (α'β) dicarboxylic anhydride at 850° (Magnanini, B 21, 2877, 22, 2502) Trimetric yellow needles (by sublimation), insol

was determined by Raoult's method Boiling

alcoholic KOH gives NC,H,Me, CO NC,HMe,CO,K

METHYL - PYROGALLOL C,HO C₆H₂(CH₃)(OH)₃ [129°] Prepared by heating the dimethyl ether with HCl to 150° Sublimes in small needles Sl sol benzene

Dimethyl ether C₆H₂(CH₃)(OH)(OMe). [36°] (265°) Crystalline Occurs together with the dimethyl ether of pyrogallol in beech wood tar oil, from which it can be isolated by means of its benzoyl compound [118°] (Hofmann, B 12, 1371) With bromine it yields C₆Br₂(CH₂)(OH)(OMe)₂ [126°] If a mixture of the sodium salts of the dimethyl ethers of pyro gallol and methyl pyrogallol is oxidised by heat in in the air or with C2Cl, eupittonic acid (pittakal) is formed

METHYL-PYROMUCIC ACID C.H.O. 18 C₄H₂MeO CO H [108°] Formed by the oxida tion of methyl furfuraldehyde (Hill, B 22, 608) and by the action of conc KOHAq upon that aldehyde (Bicler a Tollens, A 258, 125) Needles, more soluble than pyromucic acid in water, benz-With isat n and H2SO4 ene, and chloroform it gives a deep green colour on warming FeCl.

gives a biown pp

Reaction -Bromine (2 mols) added to its aqueous solution gives off CO and forms an acid C₅H₆O₅ (?acetylaciylic), which crystallises in broad flat needles [123°], S 67 (in the cold). This acid is v sol alcohol, ether, and hot water, it forms an addition product [108] with bromine, a silver salt AgC H O3, crystallising in slender needles, and a phenyl hydrazide [157°] apparently identical with that of acetyl acrylic acid (Hill a Hendrixson, B 23, 452, cf Bender, B 21, 2494, Decker, B 21, 2937)

Salt -AgC₆H₅O₅ slender needles (from hot water), sl sol hot water

DI-METHYL-PYRONE v Anhydride of Di METHYLFNE DI METHYL DIKITONI

D1-methyl-pyrone carboxylic acid v DŁ-HYDRACFTIC ACID

Di-methyl-pyrone dicarboxylic acid v Anhydrule of DI METHYLENE DI METHYL TRIKETONE v METHYL PYRROLE C,H,N & e

NMe < CHCH CHMethyl pyrroline (B), (114° 1 V) (C a D) SG 10 9203 (B) Formed by the dry distillation of methylamine mucate (C A Bell, B 10, 1866) Formed also by treating potassium pyrrole with MeI (Ciamician a Dennstedt, B 17, 2951) Liquid Resolved by heating with KOH into pyrrole and When v methyl pyrrole (3 g) is heated with MeOH (5 g), MeI (7 g), and K₂CO₃ (3 g) for 10 hours at 140° there is formed a tri methyl pyrrol (150°-165°) and penta methyl pyridine dihydride C.H.Me, NMe (Ciamician a Anderlini, B 22, 556) Methyl pyrrole acts on alloxan in warm aqueous solution forming C,H,N,O, 1e NH2 CO NH CO CO CO C4H3NMe, which crystal lises in white plates, sol hot water, sl sol alcohol and cold water (Ciamician a Silber, B 19, 1710)

r-Methyl-pyrrole dihydride C.H.NMe. Methyl-pyrroline (80°) Formed by reduction of r-methyl pyrrole with zinc dust and HOAc (Ciamician a Magnaghi, B 18, 725) Colourless, strongly alkaline liquid, miscible with water Tertiary base Its hydrochloride forms colour-less crystals.—B'_H_PtCl_ trimetric crystals, v e. sol water (Le Valle, G 15, 490)

Methylo-rodide C.H. NMe.I [286°] Obtained by the action of MeI on the above or on pyrrole dihydride (Ciamician, B 16, 1541, G 15, 492) Pearly plates Yields the platino-chloride (C₄H₆NMe₂Cl)₂PtCl₆ xaq

Methyl-pyrrole tetrahydride C.H., N . c. NMe CH, CH, Methyl pyrrolidine (82°) Formed by heating the dihydride with fuming HIAq and amorphous phosphorus at 250° (Cıa mician a Magnaghi, G 15, 493) Liquid, mis cible with water

Methylo rodeds C.H.NMe.I Formed by the action of MeI on methyl pyrrole tetrahydride or on pyrrole tetrahydride Deliquescent needles, v. e sol alcohol, insol ether and NaOHAq Ag₂O yields C₄H_sNMe₂OH, which is decomposed by distillation into MeOH and C.H.NMe Distillation of the iodide with solid

KOH yields C.H.MeNMe [89°-92°]

(a)-Methyl pyrrole C,H,N to C,H,Me NH (a) Homopyrrole (148°) Occurs, together with the (β) isomeride, in bone oil The fraction 140°-150° is boiled with KOH, and the potassium derivatives that separate are washed with ether, decomposed by water, and fractionally distilled (Ciamician, Dennstedt, a Zimmermann, B 19, 173, 2200, 22, 1918, Weidel a Ciamician, B 13, The isomerides may also be separated by conversion into their carboxylic acids, separation of these by means of their lead salts, and dry distillation of their calcium salts (Ciamician, B

Properties - Liquid, smelling like chloroform Turns brown in air Resimified by HCl, but more slowly than pyrrole, gives a white pp with HgCl₂ Forms a potassium compound C, H, MeNK, which combines with CO₂ at 200°, forming (a) methyl pyrrole carboxylic acid The potas sium compound reacts with chloroform, yielding chloro methyl pyridine Potash fusion yields pyrrole (a) carboxylic acid Oxidising agents form HOAc, ammonia, and CO₂. HCl passed into its ethereal solution ppts di methyl dipyrrole hydrochloride (C₃H,N)₂HCl, whence cold dilute H₂SO₄ forms di methyl indole (c 275°), of which the picrate melts at 156° (Dennstedt, B 21, 3439) On heating with phthalic anhydride and HOAc at 240° there is formed a yellow compound C13H2NO2 [157°], which appears to be the anhydride of an acid, which may be obtained from it by boiling with dilute KOHAq, acidifying, and extracting with ether This acid forms colourless crystals, and melts at 170°-172° (C1a-

mician a Zimmermann, B 19, 2203)
(β) Methyl-pyrrole C.H. MeNH (143°)
curs in bone oil (v supra) Liquid Reser curs in bone oil (v supra) Resembles the (a) isomeride in its reactions Potash fusion yields pyrrole (β) carboxylic acid CO₂ acting on its potassium compound forms (3) methyl pyrrole carboxylic acid HCl passed into its ethereal solution forms the hydrochloride of (3)-dimethyldipyrrole (C,H,N)2HCl, and when dilute H2SO4 is allowed to act for 24 hours on this hydrochloride there is formed a di-methyl indole of which the picrate melts at 149° (Dennstedt, B 21, 3439) On heating (3) methyl pyrrole (5 g) dissolved in

HOAc (3 vols) with phthalic anhydride (10 g) for 5 hours at 200° there is formed a compound C₁₈H₉NO₂ [215°], which may be purified by crystallisation from alcohol and sublimation, and obtained as lemon yellow needles, insol water (Ciamician & Dennstedt, B 17, 2957, 19, 2201) Dilute KOH converts the compound C13H2NO2 into an acid C13H11NO3, which forms colourless crystals (from ether), and melts at 159°

Acetyl derivative of methyl pyrrole (197°) Formed, together with C₄H₃MeNAc methyl pyrryl methyl ketone, by boiling methylpyrrole with NaOAc and Ac₂O (Ciamician a Silber, B 19, 1409) Liquid Volatile with steam, almost insol water Easily saponified by alkalis Methyl-pyrrole-tetra-hydride C,HilN 1e

CH2CHMe (97° at NH Methyl pyrrolidine CH_CH

737 mm 1 V) Formed by reduction of oxy methyl pyrrole di hydride (from γ amido valeric acid) in boiling amyl alcohol with metallic sodium (Tafel, B 20, 250) Colourless mobile liquid Very volatile at the ordinary temperature Boiling

MeI and MeOH form crystalline C₅H₁₀MeNMeI Salts (Tafel a Neugebauer, B 22, 1865) — B'HCl [210°-220°] Colourless prisms — Colourless prisms -B'2H2PtCle aq golden needles (from hot water) -B'H₂AuCl₈ [140°-144°] Golden crystals, v sol water and alcohol $-B_2'H_2C_2O_4$ [165°-168°]

Small needles

Nitrosamine CaH10(NO)N Yellow oil Methyl pyrrole tetrahydride

 $_{\rm NH}<_{\rm CH_2CH_2}^{\rm CHMe}>$ (104°) SG 2 8654 This base is formed by the dry distillation of the hydrochloride of methyl tetramethylene-diamine NH_2 CH_2 CH_2 CHMe CH_1 NH_2 (Oldach, B 20, 1657) Liquid, furning in the air, and smelling like piperidine

very deliques Salts -Hydrochloride cent - B'₂H₂PtCl₆ B'HAuCl₄ [170°] [194°] Long prisms — Minute tables, v sol water B'2HI(B113)2 -B'C6H2(NO2)3OH [105°]

(2240) Nitrosamine C₅H₁₀(NO)N

D1-methyl-pyrroleC_eH_eNie HN CMe CH>, (165°) Occurs in bone oil (Weidel a Ciamician, B 13, 78)

Formation —1 By the action of alcoholic potash at 150°-160° on its dicarboxylic ether, which is formed by reduction of a mixture of acetoacetic and isonitroso acetoacetic ethers with zinc dust and acetic acid (Knorr, B 17, 1638) -2 By heating its mono (or di) carboxylic acid, obtained from di acetyl succinic ether (Knorr, B 18, 1565)—3 By heating acetonyl acetone CH₃ CO CH₂ CH₂ CO CH₃ with a slight excess of alcoholic NH, for an hour at 150° (Paal, B 18, 2254)

Properties - Colourless liquid with unpleasant odour, almost insol water, v e sol alcohol and ether Very volatile with steam Gives a white pp with HgCl. Slowly resinified by HCl Its vapour colours pine-wood moistened with HCl red Bromine-water gives a white pp FeCl, gives a brownish red colouration H₂SO₄ added to its acetic acid solution mixed with phenan thraquinone gives a deep brownish red colour H₂SO₄ and isatin give a green colour, changing on warming to brownish red Phenyl glyoxylic acid and sulphuric acid also give a brownish-red Hydroxylamine acting on its alcoholic solution forms the di-oxim of acetonyl acetone CH₂ C(NOH) CH₂ CH₂ C(NOH) CH₃ (Ciamician a Zanetti, B 22, 3177) [136 5°]

Acetyl derivative C.H.MeNAc Liquid, not solidified at -20°, v sl sol water Saponified by potash Does not reduce AgNO, in very dilute

ammoniacal alcoholic solution

Di-methyl-pyrrole tetrahydride CaH, N 2 e NH CHMe CH2 (107° 1 V) Formed by distilling the hydrochloride of hexylene diamine NH, CHMe CH CH2 CHMe NH, obtained by re ducing the phenyl hydrazide of acetonyl acet one (Tafel, B 22, 1804, Tafel a Neugebauer, B 23, 1547) Colourless oil, smelling like pi peridine, miscible with water, alcohol, and ether Its hydrochloride crystallises in needles [188°-190°] —B',H,PtClo, small needles (from alcohol) —B',H,PtClo golden prisms
Nitrosamine C,H,6Me,N NO (135° at 60

mm) Yellow oil, lighter than water, sl sol cold water, v sol ether and alcohol Conc H2SO4 dissolves it without becoming coloured, but on warming the liquid becomes yellow and gives off The nitrosamine may be reduced to an only hydrazine, which on oxidation with HgO yields

the tetrazone C, H, N, [43°

Di-methyl-pyrrole C.H.N te

NH CH CMe (171° cor) Formed by distilling its carboxylic acid (Knorr, A 236, 326) Liquid, with blue fluorescence and characteristic sweet odour, sl sol water, v sol alcohol, ether, and benzene Its aqueous solution becomes red on warming with FeCl,

D1-methyl-pyrrole tetrahydride

 $(89^{\circ}-92^{\circ})$ Formed by distil-C,H,Me NMe ling the methylo iodide of methyl pyrrole tetia hydride with KOH (Ciamician a Magnaghi, G Liquid, miscible with water Its 15, 485) hydrochloride is deliquescent

Methylo rodide C,H,MeNMe,I needles (from alcohol), v e sol water Ppd from its aqueous solution by addition of KOH On distillation with KOH it yields trimethyl

amine and butinene C4H6

Tri-methyl-pyrrole C,H,,N (180°-195°) Occurs in bone oil (fraction 180°-205°), from which it is isolated by conversion into the potas sium compound (Ciamician a Dennstedt, B 14, Colourless oil Sol acids, sl sol water Turns brown in air Its vapour turns pine wood moistened by HCl red Reduces PtCl4 Gives a white pp with HgCl₂ Potassium acts on it very slowly with production of the solid compound C,H,oNK Cone HClAq at 120° forms ammonia and a di methyl pyridine dihydride C,H_1,N

Tri-methyl-pyrrole CH, N (150°-165°) Prepared by heating methyl pyrrole (3 g) dis solved in MeOH (5 g) with MeI (7 g) and K₂CO₃ (3 g) for 10 hours at 140° The product is acidified and distilled with steam (Ciamician a.

Anderlini, B 22, 656)

Tri-methyl-pyrrole C,H11N . e CMe CH (178° cor) Formed by heat-NMe CMe CH

304) Liquid, volatile with steam; v sol alcohol and ether Boiling aqueous FeCl, gives an intense red colour

Tri-methyl-pyrrole tetra-hydride C, H, N s.c. CHMe CH2 (116°) at 750 mm Formed CHMe CH.

by the action of MeI on NH CHMe CH. (Tafel a Neugebauer, B 23, 1549) Liquid, sl. sol water — B'HCl glittering white prisms — B'₂H,PtCl₆ yellow oil, sl sol alcohol

Methylo-rodide B'MeI [256°] less prisms, v sol water, sl sol warm alcohol

A tri-methyl pyrrole tetrahydride CH, CHMe

appears to be formed by dis CMe, CH2 tilling oxy tri methyl pyrrole dihydride with zinc dust (Weil, A 232, 213)

METHYL-PYRROLE-DISAZO- COMPOUNDS v Dis azo compounds

(α) METHYL-PYRROLE CARBOXYLIC ACID C, H, NO, te C, H, MeN CO, H (a) Homo pyrroline carboxylic acid Carbohomopyrrolic acid [169 5°] When crude potassium methyl pyriole is heated in a current of CO2 at 190° there is formed a mixture of the potassium salts of (a) and (β)methyl pyrrole carboxylic acids These acids may be separated by lead acetate, which ppts the (β) acid only (Ciamician, G 11, 230, B 14, Colourless scales, sol water Yields (a) methyl pyrrole on distillation with lime

(β) Methyl-pyrrole carboxylic acid C, H NO₂ ie C₃H₃MeN CO₂H [142 4°] Obtained as above, forms a minutely crystalline mass Its Ca salt yields (β) methyl pyrrole on distillation with

Methyl pyrrole carboxylic acid C₆H₇NO₂ * 6 C₃H₃MeN CO H [135°] Formed by heating its methylamide with alcoholic potash at 120 (Chichester A Bell, B 10, 1861, 11, 1810)

Methylamide C, H, MeN CO NHMe Formed, together with methyl pyrrole, by heating methylamine mucate in a paraffin bath (Bell) Scales or prisms, sol water, volatile with steam

Di methyl-pyrrole carboxylic acid C,H,NO, • $e \text{ NH} < \frac{\text{CMe} = \text{CH}}{\text{C(CO,H) CMe}} >$ [137°] Formed by the prolonged action of boiling aqueous KOH on tetra methyl pyrroyl pyrrole carboxylic acid or on tetramethylpyrocoll, which is itself obtained by heating di methyl pyrrole dicarboxylic acid (Magnanini, B 22, 38, Rend Accad Linc [4] 4, 475) Crystals, v sl sol cold water, dissolves in warm water with partial decomposition into CO₂ and d₁ methyl pyrrole Decomposes on Boiling Ac₂O converts it into tetramethyl pyrocoll and di methyl pyrryl methyl ketone A solution of its ammonium salt gives with lead acetate a white pp, sol excess, with cupric acetate a green crystalline pp , and with FeCl, a dark red pulverulent pp

Dimethyl pyrrole carboxyl dersvative C, H, N,O, ve CH CMe .CMe---- CMe Tetra-

ČMe NH∕ C(CO.H) CH methyl pyrroyl-pyrrole carboxylic acid. Formed ing its dicarboxylic acid at 260° (Knorr, A. 236, by boiling tetra methyl-pyrofoll with alcoholic potash, diluting with water, and ppg with acetic acid (Magnanini, B 22, 35, Rend Accad Line [4] 4, 468) At 145° it gives off CO2 and leaves a residue which may be crystallised from alcohol Boiling aqueous potash forms di methyl pyrrole carboxylic acid On warming solutions of the salts a pp of tetra methyl pyrocoll is formed. The lead and silver salts are white pps, the ferric salt a red pp, and the cupric salt a green pp -BaA'₂ Tables

green pp -BaA'₂ Tables
Methyl ether MeA' [163°] Formed from the silver salt and MeI Monoclinic tables, abc = 7011443, $\beta = 80^{\circ}59'$ sol benzene, v sol CHCl₃ Y Insol water, sl Yields MeOH and

tetramethylpyrocoll on fusion

D1 methyl pyrrolecarboxylicacid C, H, NO2 i e $NH < \stackrel{CMe}{CH} = \stackrel{C(CO,H)}{CMe} >$ [183°] Obtained from its ether, which is produced by heating the mono ethyl ether of di methyl pyrrole dicarboxylic acid NH CMe C(CO,Et) (Knorr, A Crystalline flocculi 236, 325) Split up on melting into CO2 and di-methyl pyrrole Boiling Ac₂O forms di methyl pyrryl methyl ketone CH, CO C, H, NMe, [122° [76°]

Ethyl ether EtA (291° cor) Crystalline mass, v sol alcohol and ether

Anil.de C, H2Me2N CONHPh [80°] Formed by heating the mono anilide of di methyl pyrrole dicarboxylic acid

Di methyl-pyrrole carboxylıc acıd C, H, NO, i e

CMe CH NH Obtained by saponifying CMe C CO₂H

with aqueous NaOH its ether, which is formed by heating the mono ethyl ether of di methyl-CMe C CO₂H

pyrrole dicarboxylic acid NHo CMe C CO,Et (Knorr, B 18, 1564) Slender needles Split up at 210-213° into CO, and the corresponding dı-methyl pyrrole

Salts-PbA' microcrystalline pp -AgA'

white pp

Ethyl ether EtA' [118°] 731 mm) Formed as above, and also by slowly adding cone NH, Aq to a mixture of molecular proportions of chloro acetone and acetoacetic ether Flat prisms, volatile with steam alcohol and ether, insol water

D1-methyl-pyrrole dicarboxylic acid C.H.NO.

*e NH<C(CO₂H) CMe C(CO₂H) CMe C(CO₂H) CMe Preparation—NaNO₂(2 pts) in conc aqueous solution is added to acetoacetic ether (7 pts) dissolved in HOAc Zinc dust (25 pts) is added to the well cooled product On adding water the di ethyl ether is deposited in needles, and this is saponified by boiling NaOHAq (Knorr, A 236, 817, B 17, 1638)

Properties -Crystalline flakes, v sol water and alcohol, less sol ether Rapidly turns red m air Decomposes completely at 260° into CO. and di-methyl pyrrole, without melting reduces boiling ammoniacal AgNO. It forms normal and acid salts which are mostly amor-

Mono-ethyl ether HEtA" i.s NH CMe C(CO₂Et) [202°]. Formed by

boiling the di-ethyl ether with alcoholic potash. Needles (from alcohol), sl sol cold alcohol, insol water Split up on fusion into CO2 and di methyl pyrrole carboxylic ether Its lead and silver salts are white amorphous pps When heated with Ac2O in a sealed tube at 200° it it yields NH CMe C(CO Et) [143°], and

this ether gives on saponification a crystalline acid [150°-158'], which on dry distillation is split up into CO₂ and di methyl pyrryl methyl ketone [123°] (Magnanini, B 21, 2865)

Di-ethyl ether C₁₂H₁₇NO₄ or Et₂A" [135°] Formed as above White matted needles, insol water, acids, and alkalis, sol alcohol and ether Split up by heat into CO and di methyl pyrrole Alcoholic potash forms a pp of C10H16KNO4

Mono anilide C1.H1.N2O. 1 e

NH < CMe C(CONHPh) >Formed by boiling its ethyl ether (v infra) with alcoholic potash Slender needles which soften at 180° and decompose at 198° into CO2 and the anilide of dimethyl pyrrole carboxylic acid Boiling dilute H2SO4 decomposes it in the same way

Ethyl ether of the mono-anilide C₁₄H₁₃N₂O₃Et [216°] Formed by the action of zinc dust on a mixture of equivalent quantities of acetoacetic anilide and nitioso acetoacetic ether dissolved in HOAc (Knorr, A 236, 327) Crystals, sol hot alcohol and HOAc Yields di methyl pyrrole on waiming with conc H SO4

Ethyl ether of the isomeric mono anilide C14H13N O3Etie

NH<CMe C(CO) I t) CMe [180°] Formed by the action of zinc dust on a mixture of equivalent quantities of acetoacetic ether and nitroso ace to acetic anilide dissolved in HOAc (knori) Needles (from alcohol) Yields di methyl pyrrole on warming with H2SO,

Di-anilide NH CMc C(CONHPh) CMc

[255°] Formed by the action of zinc dust on a mixture of equivalent quantities of acetoacetic anilide and nitroso acetoacetic anilide (Knori) Needles (from alcohol) Yields di methyl pyrrole on warming with H.SO

Anhydride C,H,NO, se N < CMe C(CO,H) > CMeFormed by boiling di CO

methyl pyrrole dicarboxylic acid with Ac₂O (Magnanini, B 21, 2876) Powder, almost completely insol water, alcohol, and ether Turns brown at 300° and at a higher temperature it splits up into di methyl pyrrole and tetia methyl pyrocoll -MgA'2 needles, m sol water

-Agh' yellow amorphous sediment
Ethyl ether of the anhydride
C_sH_cLtNO, [270°] Formed by boiling di methyl pyrrole dicarboxylic ether with Ac.O White, sparingly soluble needles

Di-methyl-pyrrole dicarboxylic acid

CMe C CO.H NH [250°] Formed by dis CMe C CO.H

solving di acetyl succinic ether in aqueous NH, and saponifying the resulting ether with alco holic potash (Knorr, B 18, 802, 1558) Needles (from alcohol) Decomposes at its melting point into CO₂ and $(\alpha\alpha')$ di-methyl pyrrole — BaA" small needles — CuA" 3aq slender green needles — $_{\kappa}Ag_{2}A''$ microcrystalline powder

Mono ethyl ether HEtA" [227] Siender crystals Evolves CO₂ at its melting point, giving di methyl pyrrole carboxylic acid Ithas acid properties, and its Cu, Co, and Ni salts form white felted needles

Diethylether Et.A" [99°] Colourless crystals, sol alcohol, $CHCl_3$, and HOAc, sl sol ether, nearly insol water Has weak basic and acid properties $-(C_{12}H_{17}NO_4HCl)_2PtCl_4$ Orange red crystals $-C_{12}H_{18}KNO_4$ slender felted needles

Tri-methyl-pyrrole dicarboxylic acid

saponifying with alcoholic potash its diethyl ether which is produced by boiling diaceto succinic ether with methylamine in glacial acetic acid solution (Knorr, B 18, 303, A 236, 304) Slender needles, insolwater, sl solether, solalcohol Split up at 260° into CO₁ and trimethyl pyrrole—KHA"—NH₄HA"—Ba\'—CoA'"

Ethyl ether Lt A" [72°]
Tri-methyl-pyrrole dicarboxylic acid

methyl pyrrole carboxy acetic acid [196°] I ormed by saponification by aqueous NaOH 4 q from its ether which is obtained by boiling $a\beta$ di acetyl glutaric ether with a solution of 4 NH $_{3}$ in HOAc (Knorr, B 19, 48) Slender prisms Imparts a red colouration to acidified pine wood

Dr ethyl ether Et.A" [110°] Glistening plates, v sol alcohol and ether, insol water

Tri-methyl-pyrrole tricarboxylic acid

methyl pyrrok dicarboxy acetic acid Obtained by saponifying its ether which is produced by boiling di acetyl succinic ether with glycocoll and HOAc (Knorr, A 236, 315) Crystalline pp, decomposed at 214° giving off CO₂ - K_A"' — Ag HA'" crystalline pp

Di ethyl ether Et.HA''' [169°] Formed as above Plates, insol water, v sol alcohol, ether, and alkalis -Pb(Et A'''), prisms

METHYL-PYRROLIDINE v METHYL PYRROLE TETRAHYDRIDE

METHYL-PYRROLINE v METHYL PYRROLE and its Dihydride

TETRA - METHYL - PYRROYL - PYRROLE CARBOXYLIC ACID v DI METHYL PYRROLE CARBOXYLIC ACID

DI-METHYL PYRRYL-BENZOIC ACID v
PHENYL DI-METHYL-PYRROLE CARBOXYLIG ACID
METHYL-PYRRYLENE-DIBENZOIC ACID

v DI PHENYL-METHYL PYRROLE DICARBOXYLIC ACID

v METHYL-PYRRYLENE DI METHYL DI
KETONE Q.H. NMe(CO Me). v Methyl di acetylpyrrole [134°] Formed by heating v-methylpyrrole with acetic anhydride for 8 hrs at 250°

Colouriess needles V sol alcohol, ether chloro

form, benzene, and hot water (Ciamician a. Silber, B 20, 1368, G 17, 134)

METHYL PYRRYL-GLYOXYLIC ACID

C,H,NO₃ ie NMe CH CH CH CH [142°]
Formed by boiling methyl pyrryl methyl ketone with dilute alkaline KMnO₄ (De Varda, B 21, 2871, Rend Accad Linc [4] 4, 755, 758)
Light yellow needles (from benzene) Brommadded to its solution in glacial acetic acid forms C,HBr MeN CO CO,H crystallising in yellow prisms [160°], oxidised by fuming HNO₂ to the methylininde of di bromo maleic acid—AgA' white pp

METHYL PYRRYL KETONE U PYRRYL

METHYL KFTONE

METHYL-PYRRYL METHYL KETONE

C₇H₉NO i.e NH C_{C(CO CH)}>CH [86°]
(240°) Formed by the action of Ac O and NiOAc upon methyl pyriole from bone oil (Ciamician a Silber, B 19, 1408, 20, 2604, G 16, 352, 17, 269) Small white needles (from water), v sol alcohol, ether, and benzene Not decomposed by boiling alkalis Yields a methyl pyrryl glyoxylic acid on oxidation Bromine in CS, which is oxidised by HNO, to di bromo maleic imide at −18° Animoniacal AgNO, gives with the ketone a white pp of C,H. McAcNAg

ν ΜΕΤΗΥΙ- PYRRYL ΜΕΤΗΥΙ ΚΕΤΟΝΕ

ν METHYL - PYRRYL METHYL KETONE CH, CO C, H, SMe Pseudo acetyl methyl pyrrole (201°) Prepared by boiling ν methyl pyrrole (10 g) with Ac O (70 g) and NaOAc (12 g) for 12 hours (Weidel a Ciumcian, B 13, 76, Cia mician a Dennstedt, B 17, 2952, De Varda, B 21, 2972) Colourless liquid, sl sol water Not hydrolysed by boiling KOHAq Reduces warm ainmoniacal AgNO, forming a silver mirror

Di-methyl-pyrryl methyl ketone $C_8H_{11}NO \iota e$ NH < CMe Cl1 < CMe Cl1 < CMe Cl2 < CMe Cl3 <

Di-methyl-pyrryl methyl ketone

NH CMc CH [85°] A product of the

action of Ac O on the corresponding di methyl pyrrole (Dennstedt a Zimmermann, B 19, 2195) Crystals Reduces AgNO, in very dilute alcoholic solution

DI-METHYL-PYRRYL METHYL KETONE CARBOXYLIC ACID C,H11NO, 1 e

NH CMe C(CO,H) CMe [152° 158°] Formed by saponiheation of its ethyl ether, which is prepared by heating the mono ethyl ether of dimethyl pyrrole dicarboxylic acid (1 pt) with Ac,O (8 pts) at 205° in sealed tubes (Magnanin, Rend Accad Linc [4] 4, 830, B 21, 2865) Needles (from HOAc), almost insol water and cold alcohol, v sl sol ether, CHCl₃, and benzene Completely decomposed on fusion into CO₂ and dimethyl pyrryl methyl ketone When heated with isatin and cone H,SO₄ it gives a green

A solution of its ammonium salt gives pps with lead, copper, ferric, cobalt, and mercuric salts

Ethylether EtA' [143°] Slender needles,

▼. sol hot water, alcohol, and ether

DI-METHYL-0-PYRRYL-PHENOL C,2H,NO Le [2 1] C₆H₄(OH) N CMe CH Oxy phenylde methyl pyrrole [95°] Formed by warming acetonyl acetone with o amido phenol in alco holic solution (Paal, B 19, 558) White plates (from alcohol), turning red in air, sl sol weter, v sol alcohol and ether Dissolves in alkalis, and is reppd as needles by CO2 -NaA' crystalline — The picrate crystallises in reddish brown plates

(a) METHYL-PYRRYL STYRYL KETONE C₄NH₃(CH₃) CO CH CH C₆H₅ [193°] Formed by boiling (a) methyl pyrryl methyl ketone and benzoic aldehyde with dilute caustic potash (Dennstedt a Lehne, B 22, 1918) Sulphur

yellow needles (from alcohol)

(β) Methyl-pyrryl styryl ketone C₁₄H₁₃NO 1 e C₄NH₃(CH₃) CO CH CH C₆H₅ [156°-157°] Formed from (B) methyl pyrryl methyl ketone, benzoic aldehyde, and dilute caustic potash (D a Small light yellow plates, v sol alcohol

(αβ') Dimethyl-pyrryl styryl ketone CH CMe N C CO CH CH C,H, [188°] Formed from (aB')-d1-methyl-pyrryl methyl ketone, benzoic aldehyde, and KOHAq Yellow shining plates (from alcohol) (Dennstedt, B 22, 1921)

(αβ) (?) D1-methyl-pyrryl styryl ketone CANH₂(CH₃)₂ CO CH CH C₆H₅ [166°] Formed like the preceding Small yellow plates or needles (from boiling alcohol) (Dennstedt, B 22, 1926

METHYL-PYRUVIC ACID v ETHYL GLY OXYLIC ACID Its nitrile is described as Propionyl CYANIDE

Tri - methyl - pyruvic acid C₆H₁₀O₈ CMe, CO CO₂H [88°] (185°) Formed, together with a little CMe, CO,H, by oxidising pinacolin with warm alkaline KMnO. (Glucks mann, M 10, 770) Small colourless prisms (from ether), sl sol cold water, v sol hot water, m sol ether Volatile with steam Gives a silver mirror with ammoniacal AgNOs May be reduced to CMe₃ CH(OH) CO₂H and oxidised to CMe, CO,H

Salts - NaA' - CaA', 3aq - AgA' Phenyl-hydrazide C12H16N2O2 [158°]

Long needles

METHYL-QUINALDINE v DI METHYL QUIN

METHYL-QUINALDINIUM HYDRATE v Methylo hydrate of (Py 3) METHYL-QUINOL

METHYL - QUINAZOLINE DIHYDRIDE CoH10N2 re CoH4 CH2 NH Formed by dis CMe tilling the acetyl derivative of o amido benzyl amine (Gabriel a Jansen, B 23, 2812) Colourless tenacious liquid, sol water Its solution has a bitter taste and alkaline reaction -B'HCl prisms, v sol water -B'2H2PtCl6 -Chromate reddish-yellow needles -Picrate [200°] Long needles

DI METHYL-QUINOGEN v DI METHYL DI RETONE, Reaction 6

METHYL-QUININE v QUININE METHYL-(pseudo)-QUINISATIN C10H,NO. ,co∵co

| (?) [c 120°-122°]. Formed

by exidation of $(Py \ 1 \ 2)$ di exy $(Py \ 4)$ methyl-(Py 3) pseudo oxy-quinoline

·Č(OH) C(OH) with Fe₂Cl₆ V. sol ordi-NMe CO

nary solvents Dissolves in alkalis with a vellow colour (Friedlander & Muller, B 20, 2015)

METHYL-QUINIZABIN v DI OXY METHYL-ANTHRAQUINONE

METHYL QUINOLINIC ACID v METHYL-PYRIDINE DICARBOXYLIC ACID

(Py 1) METHYL-QUINOLINE C10H2N se C_eH < N = CH >LepidineCincholepidine Mol w 143 (265°1 V) (K), (263°1 V) (D) S G 9 1 0995, 29 1 0862 (K)

Formation -1 Obtained, together with quinoline, by distilling cinchonine with aqueous KOH (Greville Williams, Pr E [3] 21, 377) — 2 By distilling the hydrochloride of quinoline tetrahydride (Py 1) carboxylic acid (tetrahydrocinchonic acid) with zinc dust (Weidel, M 3. 75) —3 Formic aldehyde or methylal is mixed with acetone, the mixture is saturated with HCl, and heated with a solution of aniline in conc HCl The bases are separated from the product by potash and fractionally distilled, the equations being $CHO + CH_3 CO CH_3 = H_2O + CH_2 CH CO CH_3$, and the following $CH_2 CH CO CH_3 + C_8H_3NH_2 = C_{10}H_3N + H_2O + H_2$ (Beyer, J pr [2] 32, 127) —4 By heating oxy-(Py 1) methyl-quinoline with zinc dust (Knorr, A 236, 94) —4 By heating cinchene with HOAc

at 200° (Koenigs, B, 23, 2677)

Preparation —1 The fraction 250°-260° of the distillate from cinchonine and KOHAq is converted into acid sulphate, the acid sulphate of (Py 1) methyl quinoline being insoluble in alcohol, whilst the acid sulphate of quinoline is soluble (Hoogewerff a Van Dorp, R T C 2, 1)

2 Obtained in pure state by the action of KOH upon cinchonine in presence of superheated

steam (Krakau, Bl [2] 45, 248)

Properties - Oil, solidifying when cooled below 0°, sl sol water, miscible with alcohol, ether, benzene, and ligroin Smells like quinoline Turns brown in air and light According to Oechsner de Coninck (Bl [2] 38, 546), two lepidines (258°) and (268°) are obtained by dis tilling cinchonine or brucine, and the base of higher boiling point alone solidifies in a freezing mixture

Reactions -1 Oxidation with KMnO, in alkaline solution gives methyl pyridine dicarb oxylic acid and, finally, pyridine tricarboxylic acid (Hoogewerff a Van Dorp, B 13, 1639) Oxidation by K₂Cr₂O, and H₂SO₄ yields quinoline (Py 1) carboxylic (cinchonic) acid -2 By adding sodium amalgam to lepidine C Greville Williams (C N 37, 85) obtained a base which formed a red crystalline nitrate C20H18N2HNOs. 3 When heated with an equivalent quantity of benzoic aldehyde and ZnCl2 it yields styrylquinoline (Heymann a Königs, B 21, 1424) -4 When heated with isoamyl iodide it yields the amylo iodide (which may be extracted by

repeatedly boiling the product with water) and also an insoluble residue whence boiling alkalis hberate 'lepamine' $C_{20}H_{22}N_2$ (Greville Williams, C. J 16, 375) Lepamine is a fragrant oil (c 275°), V D (obs and calc 10 4) Lepamine yields the salts $C_{20}H_{12}N_2H_2Cl_2$ (melting below 100°) and $C_{20}H_{22}N_2H_2PtCl_6-5$ By the action of a boiling aqueous solution of caustic potash upon mixtures of the alkylo iodides of lepidine and quinoline, blue or green substances, called cyanines are obtained (v Quinoline)

Salts -B'HCl needles -B',H PtCl, 2aq orange-red triclinic needles [226°-230°] (Knorr), [c 233°] (Königs) — B'HAuCl, [188°] Prismatic needles Decomposed when heated for some time at 110° —B'HCdCl₃ —B'HNO₃ slender prisms —B'H₂SO₄ [229°] S (alcohol) 4 at 18°, 1 1 at 78° [Krakau, J R 17, 362) —B'₂H₂Cr₂O₇ yellow needles (from hot water) which decompose at 110° — B',AgNO₃ white needles — Tartrate B'C,H,O,aq Crystallises from alcohol — Picrate B'C,H (NO₂)3OH [208°] (H a D), Small yellow needles (from [213°] (Krakau) alcoholic solutions)

Methylo rodide B'MeI [174°] Yellow prisms (from alcohol) (Hoogewerff a Van Dorp, **R** T C 2, 41, 318)

Ethylo-rodide B'EtI [143°] Isoamylo vodide B'C, H, I [160°] Yellow prisms (Hoogeweiff a Van Dorp, R T C 3, 352)

Chloro-lepidine v Chloro METHYL QUINOLINE (Pu 1)-Methyl quinoline tetrahydride

$$\mathbf{C_{10}H_{13}N}$$
 is $\mathbf{C_{6}H_{4}} < \begin{array}{c} \mathrm{CHMe} \ \mathrm{CH_{2}} \\ \mathrm{NH} \ \mathrm{CH_{2}} \end{array} >$ (250°-253°)

i V) at 740 mm Formed by adding sodium to a boiling alcoholic solution of oxy (Py 1) methylquinoline (Knorr a Klotz, B 19, 3300) also by the action of tin and HCl on lepidine Colourless oil, with pungent odour

(Py 2) Methyl quinoline
$$C_0H_1$$
 CH C(CH₃) | N CH

(250° at 710 mm) Obtained by [10°-14°] heating (Py 2) methyl quinoline (Py 3) carboxylic acid with soda lime or alone at 160° By CrO₃ and HSO₄ it is oxidised to quinoline (Py 2) carboxylic acid [273°] (Doebner a Miller, B 17, 1715, 18, 1642) Formed also by saturating a mixture of propionic aldehyde and methylal with HCl and heating the product with aniline and conc HClAq (Miller a Kinkelin, B 20, 1916) Prisms or colourless liquid

- B',H,PtCl, 2aq Salts . orange - yellow needles — B'HAuCl, [145°] Prismatic yellow needles, sol hot water, sl sol cold —Piorate B'C₆H₂(NO₂)₃OH [187°], fine yellow needles Methylo-rodide B'MeI [221°], long

[2217], yellow needles, sparingly sol alcohol

Amylo-rodide B'C, H, I [215°], yellow needles

products formed by the action of methyl iodide (In 2) methyl indole (methyl ketole) (Fischer a Steche, A. 242, 358) Oil Forms a nitros amine.

(Py 3) Methyl quinoline C10H2N 28 C.H. CH CH CM (2) Methyl-quinoline aldine (240° at 720 mm) (D a M), (246 5° 1V) at 724 mm (P a B), (240° uncor) (Drew son) Occurs in coal tar (Jacobsen a Reimer,

B 16, 1084)

Formation -1 By heating a mixture of anilme, nitrobenzene, and H.SO, with ethylene glycol or paraldehyde (Doebner a Miller, B 14, 2812) -2 By adding a little NaOH to an aqueous solution of equivalent quantities of o amido benzoic aldehyde and acetone (Friedlander a Gohring, B 16, 1835) -3 By the reduction of o nitro styryl methyl ketone with SnCl2 (Drew son, B 16, 1953) -4 By heating a mixture of aniline, aldol, and HCl (Doebner a Miller, B 16, 2464, 17, 1699) —5 By heating a mixture of aniline, acetal, and H₂SO, (D a M) -6 By heating a mixture of aniline, nitrobenzene, lactic acid, and H₂SO₄ (Wallach a Wusten, B 16, 2007) -7 By heating crotonic aldehyde with aniline, nitrobenzene, and H2SO, (Skraup, B 15, 897)—8 By distilling its carboxylic acid with lime (Beyer, J pr [2] 33, 413, Rohde, B 22, 267)—9 By heating chloro methyl quinoline (vol ii p 82) with Hi in HOAc in sealed tubes at 200° (Conrad a Limpach, B 20, 955) -10 By heating methyl indole (methyl ketole) with bromoform and alcoholic NaOH and reducing the resulting bromo methyl quinoline [78°] with P and HI at 180° (Magnanini, B 20, 2610, 21, 1940, G 17, 246) -11 By heating methyl in dole (methyl ketole) with cone HCl at 225° (Magnanin, B 20, 2609)—12 By heating ethyl acetanlide with ZnCl, at 225° (Pictet a Bunzl, B 22, 1847)

Preparation -A mixture of aniline (2 pts), puraldehyde (3 pts), and conc HClAq (4 pts), is heated on a water bath for a few hours (Doeb

ner a Miller, B 16, 2464)

Properties -Oil, smelling like quinoline, al sol water It gives with AgNO, a compound crystallising in white needles. Not affected by nitrous acid A solution of chloride of iodine in HCl forms deep yellow needles of a chloro 10dide [151°] (Dittmar, B 18, 1612)

Reactions -1 Scarcely attacked even after long boiling with chromic acid mixture, but completely exidised by CiO₃ in HOAc CrO₄ and H₂SO₄ yield quinoline (Py 3) carboxylic acid — 2 KMnO₄ oxidises it to acetyl o amidobenzoic acid (Doebner a Miller, B 15, 3075) -3 Cold cone HNO₃ forms (B 3) and (B 4) nitro (Py 3) methyl quinolines Boiling cone HNO, forms nitro quinoline carboxylic acid [220°] —4 Tin and HCl reduce it to a tetra hydride -5 On heating with sulphur H.S is evolved and the product contains a base C .H 16N aq [162°] which crystallises from alcohol in white needles (Von Miller, B 21, 1828) -6Combines at once with formamide forming a white mass, which crystallises from alcohol or ether in needles of C.H.MeN C(OH)NH2 [76°], and is decomposed by water (Clève, B 20, 76) 7 Combines with aldehydes, forming aldol like products which readily split off water (Von Miller, B. 20, 2041) Thus paraldehyde when heated with quinaldine for 5 hours at 210° yıelds (Py 3) allyl quinoline (249°-253°) (Eisele, B. 20, 2043), isobutyric aldehyde with ZnOl. forms $C_{14}H_{17}NO$ [93°] (Brünner, B 20, 2041); p nutro benzonc aldehyde at 120° unites forming C,H,N CH2 CH(OH) C,H,NO2 [160°] which when heated with Ac₂O loses water and becomes p nitro styryl quinoline (Bulach, B 20, 2046, B 22, 285) In like manner, when quinaldine (1 mol) is heated with furfuraldehyde (1 mol) and a little ZnCl2 for 2 hours at 100° the product is C,H,N CH CH C,H,O which crystallises from ligroin in tufts of needles (Srpek, B 20, 2044) 8 When heated with phthalic anhydride and ZnCl₂ at 200° it yields 'quinoline yellow' C₉H_bN CH C₂O₂ C₆H₄ which crystallises from alcohol in golden needles [235°], may be sub hmed, and is insol water, v sl sol ether, m sol boiling alcohol, v sol HOAc It dyes silk and wool yellow (Jacobsen a Reimer, B 16,

Salts -The nitrate and hydrochloride sare easily soluble — B'₂H₂PtCl₆ [226°] (Fa G), [229°] (Pa B), [230°] (Beyer) Sparingly soluble orange prisms — Aurochloride yellow crystalline pp —B'HHgCl₃ [165 5°] White needles —B'HI [186°] V sol water — B'H SO, [213°] Deliquescent prisms (Hooge werff a Van Dorp, R T C 3, 344) —B',H,Cl.,O long yellowish ied needles, sol hot, al sol cold. water -Picrate B'C, H (NO,), OH [191°] Needles, sl sol water and cold alcohol

Methylo-rodide B'MeI [195°] Lemonyellow needles, v sol water, sol alcohol, insol ether Yields (B'MeCl) PtCl4 crystallising in orange tables, (B'MeCl)AuCl, crystallising from hot water in lemon yellow needles, and (B'Me)₂Cr₂O₇ crystallising in orange plates, sl

sol water, exploding at 90°

Methylo oxide (B'Me)₂O Formed by adding aqueous KOH to the methylo iodide (Bernthsen a Hess, B 18, 32, Moller, A 242, 302) Yellow amorphous flakes, sl sol water, v sol alcohol and ether Easily decomposes, becoming red HIAq converts it into B'MeI,

while HCl yields B'MeCl

Ethylo rodide B'EtI Ethyl quinaldin-[234°] um vodide Prepared by heating quinaldine with EtI at 100° Yellow prisms (from alcohol), decomposed on fusion (Hoogewerff a Van Dorp, R T C 3,345,350, Spaltholz, B 16, 1851) Aqueous KOH converts it into the flocculent oxide (B'Et)20 which readily changes The on exposure to air to a crimson resin oxide yields the following salts B'EtAuCl, golden needles - (B'EtCl)₂PtCl ruby 1ed prisms, sol hot water — (BEt), Cr, O, Reddish yellow needles, exploding at 100° On heating quinoline ethylo iodide (2 pts) with quinaldine ethylo iodide (1 pt) and aqueous KOH diethyl isocyanine iodide is formed, which crystallises from its crimson alcoholic solution in lustrous green prisms (v Quinoline)

Propylo rodide B'PrI [167°] Obtained by heating its components on the water bath (Moller, 4 242, 306) Small greenish yellow prisms (from alcohol), sl sol cold, v sol hot, alcohol and water Gives with aqueous KOH a yellow amorphous oxide (B'Pr),0, sol alcohol and ether It yields the salts—(B'PrCl)₂PtCl₄ crystallising in orange plates, B'PrAuCl₄ crystal lising in canary yellow needles, v sl sol cold water, and (B'Pr)2Cr2O, crystallising in brownish

red prisms

Isobutylo-rodide B'C,H,I [172°] Ob tained by cohobating its components at 115° (M). Straw yellow plates, sol hot alcohol Yields an unstable oxide which on heating changes to a violet colouring matter

Isoamylo-rodide B'C,H,I Formed by cohobating its components for 12 Small yellow prisms, v sol hours at 145° water and hot alcohol Converted by aqueous KOH into an oxide which condenses to a crimson dye on heating

(Py 3)-Methyl-quinoline tetrahydride CH₂ CH₂

Tetra hydro quinaldine

C,H **\NH** СНМе Formed by reducing (248° at 710 mm) CH, CO CH CH2 C, H, NO2 [1 2] (Jackson, B 14, It is also a product of the action of HCl on a mixture of aldehyde and aniline (Doebner a Miller, B 17, 1698) Prepared by reducing quinaldine with tin and HCl (Docbner a Miller, B 16, 2467) Colourless liquid with pleasant smell, sl sol water, v sol alcohol, ether, and FeCl_s gives a blood red colour to benzene aqueous solutions of its salts, CrO3 acts in like Nitrous acid produces an oily nitros amine and a crystalline nitro nitrosamine [152°] (Moller, A 242, 314) Heated with benzotii

ν Methyl quinoline dihydride C₁₀H₁₁N ι e C₆H, CH CH NMe CH₂ This base is probably formed by heating v methyl indole with MeI (Fischer

chloride it gives a green dye stuff -B' H PtCl,

a Steche, B 20, 2201)

yellow needles

ν Methyl quinoline tetrahydride C₁₀H₁₃N ι e $C_6H_1 < \begin{array}{c} CH_2 & CH_2 \\ NMe & CH_2 \end{array}$ Kairoline (243° at 720 mm) Prepared by heating quinoline tetrahydride with Mel (Hoffmann a Konigs, B 16, 731), or by ie duction of quinoline methylo iodide with tin and HCl, the yield by the latter process being of p c of the theoretical (Feer a Konigs, B 18, 2388) Resembles quinine in physiological action, and has been used as a febrifuge Nitrous acid gives a yellowish red colouration in dilute solu-Gives a green dye stuff on heating with tions benzo trichloride

Salts -B'HClaq $\lceil 244^{\circ} \rceil$ Prepared by heating quinoline tetrahydride with MeOH and conc HClAq at 160° (Ostermayer, B 18, 595) Crystallises from alcohol or chloroform in tetra hedra, v sol alcohol, sl sol ether -B'HCIICI [86°] Large yellow needles -B'H,PtCl, [177°] Red crystalline pp —Picrate [125°] yellow needles

Nitroso derivative C10H12(NO)N Green plates, v sol alcohol, ether, and benzene, sl sol ligroin Does not give Liebermann's reac Not affected by boiling NaOHAq

Methylo hydroxide *B'MeOH Strong alkalıne base, sol water

C.H. NMeEtI Ethylo-rodide [179°] Formed from ethyl quinoline tetrahydride and MeI (Claus a Stegelitz, B 17, 1331) Crystals With Ag O it gives a Not affected by KOHAq V sol water, insol ether crystalline base (C₀H₁₀MeEtCl)₂PtCl₄

References - Amido methyl hydro quinol INE, NITRO METHYL QUINOLINE TETRAHYDRIDE, and

OXY METHYL QUINOLINE TETRAHYDRIDE

(B 1) Methyl quinoline $O_{1e}H_{s}N$ s.e. CH CMC COH CH
CH CM CN CH
(251°) This is probably the constitution of the base which is formed, together with (B 3) methyl quinoline, by heating m toluidine, o nitro phenol, glycerin, and $H_{2}SO_{s}$ together (Skraup a Brunner, M 7, 139) Its acid sulphate is more soluble in alcohol than that of the (B 3) isomeride The platinochloride melts at 224°, the picrate at 198° The picrate is much less soluble than that of the accompanying isomeride The chromate is v sol water

Derivative - v Chloro (B 1) methyl quinol NE, which may, however, perhaps be Chloro

(B 3) METHYL QUINOLINE

(\$\hat{B}_2\$) - Methyl - quinoline \$C_{10}H_0N\$ is \$C_{10}M_0CH CCHCH\$ proluquinoline (258°) at 745 mm \$S_0G_2\$1 0815 , \$\hat{20}_2\$1 0681 Formed by heating a mixture of ptoluidine, p introtoluene, glycerin, and \$H_2SO_4\$ (Skiaup, \$M_2\$, 158) Liquid, smelling like quinoline \(\hat{11}_2\$ index pyridine di carboxylic (quinoline) acid on oxidation with \$KMnO_4\$ HOCl forms chloro oxy methyl quinoline \$C_0H_3Me\subseteq CHCH\$

Salts—B'HCl aq slender needles, v sol water and alcohol—B' H PtCl, 2aq slender yel lowprisms—B HI [186°] (Moller, A 242, 307)—B'H₂SO₄ aq Piisms, v e sol water—Picrate

B'H₂SO₄ aq Phisms, v e sol water—Piera te B'C₄H (NO₂)₃OH [229°] Yellow powder Chloro vodide C₁₀H₃NICl [c 170°], easily soluble in alcohol The hydrochloride C₁₀H₂NICl, HCl is formed by adding a solution of chloride of iodine in HCl to a solution of (B 2) methyl quinoline It forms easily soluble reddishvellow needles [c 112°], blackened by NH₃ (Dittmar, B 18, 1612)

Methylo rodide B'MeI Slender yellow 1sh prisms When heated with (Py 1) methyloquinoline methylo 1odide, and aqueous KOH it forms'd methyl methylo cyanine' C., H., N., I 2aq, which crystallises from alcohol in violet blue needles, sl sol water, melting (when anhydrous) at 270°–277° (Hoogewerff a Van Dorp, R T C 3, 342)

Derivatives -V Tri chloro (B 2) mi thylquinoline, Chloro oxy (B 2) methyl quinoline, Di chloro di nitro oxy (B 2) methylquinoline, and Oxy (B 2) methylquinoline,

(B 3) Methyl - quinoline C₁₀H₂N ie сн сн сн сн (250° m Toluquinoline CMe CH C N $_{
m CH}$ uncor), 259 7° cor at 747 mm) SG 91 0839, 20 1 0722 Formed, together with smaller quantities of an isomeride, probably (B 1) methylquinoline, by heating a mixture of m toluidine, m nitro toluene, glycerin, and H2SO, (Skiaup, M 3, 381, B 15, 893), or of m toluidine, o nitrophenol, glycerin, aud H SO, (Skraup a Brunner, The two bases may be separated by M 7, 139) crystallising their acid sulphates from alcohol, in which the sulphate of the base here described is the less soluble Yellowish, highly refractive liquid, not solid at -20° Yields on oxidation quinoline (B 3) carboxylic acid [247°]

Salts —Hydrochloride large transparent prisms —B'H.PtCl. 2aq [224°] Orange prisms —B'H.8O. —B'.(H.8O.). xaq —Chromate [89°]; v. al. sol water — Picrate.

[287°].

Methylo-sodide B'MeI 12aq golden needles

Salts—B'HCl2}aq very soluble transparent prisms—B'₂H₂PtCl₆ 2aq orange prisms—B'H₂SO, prisms, sl sol cold, v sol hot, water—B'C₆H₂(NO₂)₅OH [200°] Pale yellow leaflets

Methylo-vodide B'MeI Crystalline powder

(B~4) - Methyl - quinoline tetrahydride $C_{16}H_{14}N$ Oil Obtained by reducing (B~4) methyl quinoline (Ziegler, B~21,~866)

Nitiosamine C_bH₅MeN NO Formed by treating (B 4) methyl quinoline tetrahydride with NaNO₂ and HOAc (Ziegler) Oil Slowly converted by alcoholic HCl into an isomeric nitroso derivative, which crystallises from benzene in lustrous steel blue crystals [140°], and may be reduced to an amido (B 4) methyl quinoline tetrahydride, giving a hydrochloride melting at 166°

(B 2, 4) Di-methyl-quinoline C₁₁H₁₁N is COMe CH | C₃H₄N (268° cor) SG z 10665 CH CMe Formed by heating (1, 3, 4) m xylidine with glycerin, nitrobenzene, and H SO₄ (Behnend, B 17, 2716) Colourless oil Yields a sulphonic acid melting at 166° — B',H,PtCl₈ yellow

needles—B'H SO, minute needles Its bi
chromate forms long yellow needles
(B 1, 2) or (B 2, 3) Di methyl-quinoline
CMe CMe
CMe CMe
CMe CH

C₅H₂N or |

C₃H₂N (274°)

CH CH

Obtained by heating a mixture of o xylidine

C.H.Me.(NH.) [1 2 4], nitrobenzene, glycerin,
and H.SO. (Berend, B 17, 1139) – B'.H.PtCl., aq
minute yellow needles — B'H.SO., raq glistening
pisms — B'H.Cr.O., slightly soluble orange

(B 1, 4) Di-methyl-quinoline C₁₁H₁₁N co CH CMe C₅H₂N [5°] (265°) at 736 mm S G

CH CMe

To 1752 (B), 21 1070 Formed by warming the sulphate of p xylidine C,H,Me (NH.) [1 4 2] with nitrobenzene and glycerin (Berend, B 18, 3165, Lellmann a Alt, A 237, 308) Oxidised by dilute HNO3 at 170° to (B 4) methyl quinol ine (B 1) carboxylic acid—B'2H,2tCl, yellow needles—B',H,Cr,O, [149°] Orange needles

Tetra hydride C,H,S,N (271°) Formed

Tetra hydride C₁,H₁,N (271°) Formed by reduction with zinc and HCl (Berend, B 18, 3165) Pleasant smelling liquid — B'HCl slender needles (from alcohol) or six sided plates (from water)

(B 4, Pý 3) Di-methyl-quinoline C₁₁H₁₁N 2 6 CH CH C CH CH

CH.CMe C N CMe

(252°) Formed by heating a mixture of o tolu idine, paraldehyde, and HClAq at 100° (Doebner a Miller, B 16, 2469) Formed also by heating its carboxylic acid with KOH (Panajotoff, B 20, 40) Colourless liquid, v sol alcohol and ether, al sol water Volatile with steam -Platino chlorides B', H.PtCl, 2aq dark yellow needles -B'2H2Cr2O, orange yellow needles, sol hot, sl sol cold, water On oxidation with chromic acid it yields an acid $C_{11}H_0NO_2$ identical with that obtained from o amido benzoic acid and aldehyde (Von Miller a R Meyer, B 23, 2260)

Methylo rodrde B'MeI [221°] Prepared by heating the base with MeI at 100° (Möller, A 242, 309) Lemon yellow needles (from in-Alkalıs liberate an unstable base, which on heating yields the original o methyl quin aldine It also yields the salts (B'MeCl)2PtCl crystallising in yellow needles, v sl sol cold water, B'MeAuCl₄, and (B'Me)₂Cr₂O₇ crystallising

from water in orange plates

Ethylo vodide B'EtI [229°] From the base and EtI at 140° (Moller) Lemon yellow needles (from alcohol) Yields the salts (B'Et), PtCl, crystallising in orange yellow needles, and B'LtAuCl, crystallising in lemonyellow plates, m sol hot water

CH, CH, Tetrahydride C.H.Me NH CHMe

Tetrahydro methyl quinaldine (261°) Formed by reducing (B 4, Py 3) di methyl quinoline (Doebner a Miller, B 16, 2469) Colourless liquid Gives a red colouration with FeCl3 - $B_2^IH_2PtCl_a$ concentric red needles (B 3, Py 3) Di-methyl-quinoline $C_{11}H_{11}N$ is

CH CH C CH CH

m Methyl quinaldine CMe CH C N CMe [61°] (264°) Formed by heating a mixture of m toluidine, paraldehyde, and HCl (Doebner a Miller, B 16, 2471) Long colorrless needles v sol alcohol, ether, and benzene, sl sol water Oxidised by chromic acid to methyl quinoline m-carboxylic acid [284°] (Miller a Rist, B 23, 2263, 3483) $-B'_2H_*Cr_2O$, thick orange needles, nearly insol cold water $-B'_2H_*PtCl_\bullet$ small yellow needles

(B 2, Py 3) Di-methyl-quinoline

CMè CH C ČH CH

p Methyl quinaldine [60°] CH CHC N CMe

(D a M), [55°] (Jacobsen a Reimer, B 16, 2603) (266°) (D a M), (260°) (J a R) Formed by heating a mixture of p toluidine, paraldehyde, and HCl (Doebner a Miller, B 16, 2470) Large colourless trimetric prisms, smell ing like anise seed V sol alcohol, ether, and benzene, sl sol hot water Oxidised by chromic acid to methyl quinoline p carboxylic acid [256°] (Miller a Schunck, B 23, 2263) Heated with phthalic anhydride and ZnCl, at 200° it yields methyl-quinophthalone or methyl-quinoline yellow C₁₁H₆N C₂O₂ C₆H₄ [203°] which crystal-lises from alcohol in golden needles (J a R) — B'2H2PtCl, nearly colourless slender needles, sl sol. hot water — B'₂H₂Cr₂O₇ long yellow needles, m sol hot water — The hydro chloride, nitrate, sulphate, and acetate, are easily soluble crystalline salts

Methylo rodide B'MeI. [237°] Formed

from the base and MeI in the cold (Möller, A. 242, 311) Lemon yellow needles, sl sol cold alcohol, insol ether, v sol water Yields the salts (B'Me)₂PtCl_e, B'MeAuCl_e, and (B'Me)₂Cr₂O₇, all three crystallising in needles

Tetrahydride C.H.Me CH, CH, CHMe Formed by reducing the base with tin and HCl (Doebner a Miller, B 16, 2471) Liquid, sl sol water, v sol alcohol and ether Its aqueous solution is coloured blood red by FeCl,

(B 4, Py 1) Di-methyl-quinoline

CH CH C CMe CH (274° 1 V) Formed by CH CMe C N CH distilling oxy (B 4, Py 1) di methyl quinoline with zinc dust (Knorr, A 245, 369) yellow oil with pungent taste and smell, v sol alcohol and ether, almost insol water B'₂H PtCl₆ aq [220°] —B'HAuCl₄ [181°]
(B 3, Py 1) Di-methyl-quinoline
CH CH C CMe CH
(c 283° 1 V) Forme

(c 283° 1 V) CMe CH C N CH by distilling (Py 3) oxy (B 3, Py 1) di methyl quinoline with zinc dust (Knoir, A 245, 371) Oil, volatile with steam —B'2H,PtCl, 2aq [227°]

Reddish brown prisms

(B 2, Py 1) Di methyl quinoline CMe CH C CMe CH CH CH C N CH (γ) Methyl p toluquinoline (280° 1 V) Formed by distilling $(P_{ij} \ 3)$ oxy $(B\ 2,\ Py'\ 1)$ di methyl quinoline with zinc dust (Knorr, A 245, 366) Pungent oil, v sol alcohol and ether Oxidised by chronic acid to a methyl quinoline carboxylic acid (Von Miller a Daniel, B 23, 2264)—B',H,PtCl, 2aq needles, decomposing at 231°—B',HAuCl, needles, decomposing near 192°—B',H Cr,O, needles, decomposing near 150°—B',C,H,(NO),OH needles, decomposing near 230°

Formed by adding tiglic aldehyde (1 mol) to a mixture of aniline hydrochloride (1 mols) and HCl heated to 85° (Rohde, B 20, 1912, 22, 268) Formed also in small quantity by heating a mixture of acetic and propionic aldehydes with aniline and HClAq at 100° Tables or plates, v sl sol water, v sol ether, v e sol alcohol Chromic acid mixture oxidises it to (Py 3)methyl quinoline (Py 2) carboxylic acid On condensation with benzil, by heating at 100° for 24 hours, it yields a base [176°], of which the solutions of the salts exhibit green fluorescence This base changes on heating for some time at 180° to a polymeride [240°]

Salts—B'HCl 2aq radiating needles, v e sol water and alcohol—B'_HPtCl, 2aq orange needles, turning black at 230°—B'HNO, prisms, v e sol water and alcohol—B'H_2SO, aq. [235°] slender radiating needles, v e sol water, m sol alcohol -B'2H2Cr2O, long orange needles, m sol hot water, turns brown at 150° Picrate:

 $[225^{\circ}]$

Methylorodide B'MeI aq [218°] Sicklelike groups of needles (from alcohol), m sol. water and alcohol

(Py 1, 2) D1-methyl-quinoline C_eH CMe CMe [65°]. (290° 1 V) at 737 mm. formed by distilling (Py 8, 2, 1) oxy di methylunnoline with zinc-dust (Knorr, A 245, 362). In oxidation by chromic acid mixture it yields Py 2)-methyl quinoline (Py 1)-carboxylic acid Seitz, B 23, 2257) — B'H-PtCl, 2aq [240°] — 3'HAuCl, [177°] Plates — B'2H-Cr₂O, red ieedles — Piorate B'C₆H₂(NO₂)₂OH [c 205°] **Yellow** needles

Methylo-rodide B'MeI [191°] Light-

ellow needles (from alcohol)

(Py 1, 3) Di-methyl-quinoline

J.H. CMe CH (264° uncor) SG 151 061

Formation -1 By saturating a mixture of paraldehyde (120 g) and acetone (200 g) with taseous HCl, allowing the mixture to stand for i day or two and then pouring it slowly into a solution of aniline (200 g) in conc HClAq (400 g) in this reaction the ketone CH, CH CH CO CH, s doubtless first formed (C Beyer, J pr [2] 32, 125, 33, 401) -2 Together with methane, by reating acetone with aniline hydrochloride at 180, the yield being 3 pc of the theoretical Riehm, A 238, 3, B 18, 3296)—3 Together with the base C.H.N.CMe₂ (228°), V D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), V D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), V D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), V D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), V D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), V D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), V D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), V D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), V D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), V D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), V D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), V D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), V D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), V D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), V D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), V D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), V D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), V D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), V D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), V D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), V D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), v D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), v D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), v D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), v D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), v D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), v D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), v D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), v D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), v D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), v D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), v D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), v D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), v D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), v D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), v D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), v D 66 4 (calc. 186.5), and C.H.N.CMe₂ (238°), and C.H.N.CMe₂ (238°), and C.H.N.CMe₂ (238°), and C.H.N.CMe₂ 36 5), and C₁, H₁₃N(?) (275°), by heating aniline with acctone and a dehydrating agent such as ZnCl₂ or P_2O_3 —4 By heating aniline with mesityl oxide at 180° (Engler a Riehm, B 18, 2245) — 5 By heating acetanilide with acetone, yield being 8 pc of the theoretical -6 From acetone and benzamilde -7 By the action of NaOHAq on a mixture of o amido acetophenone and acetone (O Fischer, B 19, 1037) -8 By dissolving the anilide of methylene di methyl diketone (acetyl acetone) in conc H2SO4, warm ing, diluting with cold water, and neutralising with NH₂ (Combes, C R 106, 142)

Properties -Oil, with sweetish smell, somewhat like quinoline, volatile with steam Not

affected by nitrous acid

Reactions —1 CrO₃ oxidises it to (Py 3)-methyl quinoline (Py 1) carboxylic acid —2 By heating with phthalic anhydride and a little ZnCl₂ at 200° it is converted into a 'phthalone' C₁₁H₉N C₂O₂ C₆H₄, which crystallises from alco hol in orange needles [238°] (Beyer, J pr [2] 83, 407)

Salts -B'HCl slender, stellate flat needles (by sublimation), v sol water and alcohol—B H₂PtCl₆ [229°]—B₂H₂PtCl₆ 2aq—B' H₂ZnCl₄ 1½aq—B'H₂SO₄ [225°-228°] Concentric needles, v sol water, sl sol alcohol— B' H2Cr2O, [172°] Orange needles, v sol hot, v sl sol cold, water —B'C₆H₂(NO₂)₃OH [190°] Needles (from acetone)

Methylo wodide B'MeI [226°]

Ethylo rodids B'EtI [214°]. Needles

(from alcohol)

D1-methyl-quinoline CaH4(O3HMe2N). [65°] (267°) at 713 mm Occurs among the products of the action of aniline on a mixture of isobutyric aldehyde, methylal, and HCl (Von Miller a Kinkelin, B 20, 1937) Monoclinic prisms-B'₂H₂PtCl₂ 2aq [268°] Groups of needle (from HClAq)—B'C₈H₄(NO₂)₂OH [220°] A needles gregates of tables (from hot alcohol)

(Py 1, 4) Di-methyl-quinoline tetrahydride C.H. CHMe CH. (255° 1.♥). Formed by adding Na to a boiling alcoholic solution of oxy-

VOL III

(Py 1, 4)-di-methyl-quinoline (methyl-lepidone) (Knorr a Klotz, B 19, 8802) Colourless liquid (Py 3 4) Di-methyl-quinoline tetrahydride

C.H. CH2 CH2. (248°) at 710 mm Formed by heating (Py 3) methyl-quinoline tetrahydride with MeI (Doebner a Miller, B 16, 2468) Formed also by reducing the methylo iodide of (Py 8) methyl quinoline with tin and HCl (Feer & Königs, B 18, 2388) Colourless liquid On heating with benzotrichloride it gives a green dye stuff -B'2H2PtOl sparingly soluble red granular pp

Methylo-todide B'MeI. [205°] Colour less needles, v e sol water and hot alcohol, insol ether (Moller, A 242, 318) Not acted on by alkalis, but converted by moist Ag2O into the ammonium base, which is split up by distilla tion into MeOH and (Py 3, 4) di-methyl quinolme Yields the salts (B'Me) PtCl crystallising from water in small brick-red crystals, B'MeAuCl, crystallising in lemon yellow needles, and (B'Me), Cr.O, crystallising in small hexagonal plates

Di methyl-quinoline C₁₁H₁₁N (245°) Occurs in commercial quinaldine (Einhorn, B 18,

3144) -B'2H2PtCl6 [238°

(Py 1, 2, 4) Tri-methyl-quinoline dihydride C₁₂H₁₅N s.e C₆H₄< CMe CMe CH₂ (244° 1 V) at 746 mm Formed by heating methyl indole (methyl ketole) C₆H₄<\(\frac{CH}{NH}\)>CMe with MeI and a little MeOH for 20 hours at 100° (Fischer a Steche, B 20, 818, A 242, 353). Formed by heating (In 1,2) di methyl indole with MeOH and MeI in sealed tubes at 100° (Fischer a Steche, A 242, 364, Wolff, B 21, 125) Formed also by heating indole with MeI, MeOH, and Na CO, at 130° (Ciamician a Zatti, B 22, 1980. Zattı a Ferratını, B 23, 2302, Fischer a Meyer, B 23, 2631) Formed likewise by heating B 23, 2631) Formed likewise by heating scatole (1 pt) with MeI (2 pts) and MeOH (1 pt) for 12 hours at 130° (F a M) Oil, turning red in air, miscible with alcohol, ether, benzene, and chloroform Nitrous acid gives a reddish brown oil, becoming crystalline FeCl. added to its solution in HClAq ppts golden yellow plates or needles of a compound v sol.

hot water, v sl sol conc HClAq Salts — The hydrochloride is v water -Platinochloride [c 212°] -B'H2SO4 plates —B'HI [253°] Prisms (from alcohol) — B'C₆H₂(NO₂)₅OH [148°] Golden-yellow needles

(from alcohol)

(Py 1,2,4) Tri-methyl-quinoline tetrahydride C₆H₄ CHMe CHMe (?) (239° 1 V) at 749 mm Formed by reducing the dihydride with zinc and HClAq (Fischer a Steche, A 242, 356) Colour less liquid, sl sol water, v sol ether, alcohol, and benzene FeCl, gives a brown amorphous pp in its solution in HClAq—Picrate [162°] (F a S), [164°] (Ciamician a Zatti, B 22, 1981), yellow plates (from alcohol) —Platino-ohloride bright-red crystals

Methylo-rodide B'MeI [251°]. Plates

or needles (from alcohol), m sol water

(Py 1, 3, 4) Tri methyl-quinoline tetrahydride C.H. CHMe CH. NMe CHMe Hydro-10dide B'HI [215°] Formed from (Py 1, 3)-dimethyl-quinoline by reducing in alcoholic solution with Na and heating the product with MeI and MeOH at 100° (Fischer a Meyer, B 23, 2681).

(Py. 1, 2, 4)-Tri-methyl-quinoline tetrahydride C.H. CHMe CHMe. Hydro-10dide B'HI. [205°] Formed like the preceding from (Py 1, 2)-di methyl-quinoline (F. a. M). Crystalline

(B 2,4, Py 3) Tri-methyl-quinoline C₁₂H₁₃N ve CMe CH CH CH CH op Di methyl quinaldine [46°] (260°) at 719 mm Formed by heating m-xylidine with paraldehyde and conc HClAq on the water-bath (Panajotoff, B 20, 32) Small plates (from alcohol) or monoclinic prisms (from petroleum-ether), insol water, ve sol alcohol Readily volatile with steam Yields on oxidation (B 4, Py 3)-di-methyl-quinoline (B 2) carboxylic acid Forms, with chloral, a compound C₁₄H₁₂Cl₂Naq, melting at 108°, and crystallising in yellowish needles, v sol alcohol

Salts —B'HCl white needles —
B'_zH₂PtCl_z 2aq orange-yellow needles, sl sol water —B'H₂SO_z aq white needles, v sol water and alcohol, sl sol ether —B'HNO_z transparent trichine prisms —B'₂H₂Cr₂O₇ orange yel low needles —B'C_zH₂(NO₂)_zOH [185°] Yellow needles

Methylo-vodide B'MeI aq Yellow needles, v sol water

Tetrahydride C₈H₂Me₂ CH₂ CH₂
NH CHMe^{*}

(200°-250°) Formed by reducing the base with tin and HCl (P) -B'_2H_2PtCl_s orange plates (B 1 or 3, 2, Py 3) Tri-methyl-quinoline CMe CMe C CH CH or CMe CH C CH CH

CMe CMe C CH CH or CMe CH C CH CH CH CH CH CH C N CMe or CMe CH C N CMe Formed from oxylidine, aldehyde, and HCl (Merz, B 17, 1158) Monoclinic crystals—B'_H_PtCl_a minute needles

[64°] (P), [40°] (C); (278°) (P), (281°) (C) Formed by saturating a mixture of acetone (40 g) and paraldehyde (30 g) with HCl at 0°, allowing to stand 12 hours in a freezing mixture, pouring into a solution of ptoluidine (65 g) in furning HClAq (130 g) and heating on the water bath for 7 hours (Pfitzinger, J pr [2] 38, 41) Formed also by dissolving the p-toluide of methylene di-methyl diketone CM, CO CH, C(NC,H,Me) CH, in cone H,SO, warming, diluting, and neutralising with NH. (Combes, C R 106, 145) White needles, containing water of crystallisation which is given off in a desiccator, the anhydrous base crystallising in tables and absorbing water (1 mol) from the air Sl. sol water, v sol alcohol, ether, and petroleum-ether. Volatile with steam.

It has a bitter, acrid taste, and an irritating vapour

Salts—B'HCl 2aq white needles, v e sol hot water and alcohol [260°]—B'₂H₂PtCl₂2aq yellow needles, v sl sol water, almost insol alcohol [220°] (C)—B'H₂SO₄ [222°] White needles or rhombohedra (containing aq), m sol cold alcohol—B'₂H₂Cr₂O, Yellowish red needles, v sl sol cold water—B'C₂H₂(NO₂)₂OH [201°] Greenish-yellow needles (from hot acetone)

Methylo-rodide B'MeI [226°] Needles (containing aql, sol water, alcohol, and ether (B2, Py 2, 3) Tri-methyl-quinoline CMe CH C CH CMe (B2, Py 2, 3) Tri-methyl-quinoline

CMe CH C CH CMe [87°] (285°) Formed CH CH C N CMe [87°] (285°) Formed from tiglic aldehyde (1 mol), p toluidine (4 mols) and HCl (8 mols) (Von Miller a Ohler, B 23, 2268) White nodules (from ligroin), insolwater, m sol ligroin, v sol ether Yields on oxidation (Py 2, 3) di methyl quinoline (B 2)-carboxylic acid [270°]

Salts — B'.H.PtCl, 2aq lamınæ — The chromate crystallises in orange lamınæ, v sl sol water —The hydrochloride and sulphate are v e sol water —Picrate [212°] Straw colouredliamınæ

(B 4, Py 1,3) Tri-methyl-quinoline CH CH C CMe CH (280°) Formed by the CH CMe.C N CMe (280°) Formed by the action of H,SO₄ on the o toluide of methylene dimethyl diketone CH₃ CO CH₂ C(NC,H₂) CH₃ (Combes, C R 106, 145) Oil—Platinochloride [257°]

(B 4, Py 3, 4)-Tri-methyl-quinoline tetra hydride CH CH C CH₂ CH₂ (244°) Formed by the action of MeI on (B 4, Py 3) di methylquinoline tetrahydride (Doebner a Miller, B 16, 2470) Colourless liquid

(Py 1, 2, 3) Tri-methyl quinoline

 C_bH_4 CMe CMe [65°] (285°) Formed by heating the anilde of di methyl ethylidene dike tone CH₄ CO CHMe C(NC,H₃) CH₄ with H₂SO₄, and separated by passing NH₂ through the diluted product (Combes, C R 106, 144) $-B'_2H_2PtCl_6$ [215°]

Tri-methyl-quinoline C₁₂H₁₈N (270°-280°) A by product in the preparation of quinaldine from paraldehyde, aniline, and HCl (Doebner a Miller, B 18, 8352) — B'₂H₂PtCl₆ 2aq paleyellow needles

(B 1, 2, 4, Py 3)-Tetra-methyl-quinoline CMe CMe C CH CH CH CMe C N CMe [c 20°] (800°) Formed by heating solid ψ cumidine [63°] with par aldehyde and HClAq at 105° (Doebner a Miller, B 17, 1710) Crystalline, v sol alcohol and ether, insol water —B'₂H₂Cr₂O₇, long yellow needles

(B 2, 4, Py 1, 8)-Tetra-methyl-quinoline CMe CH CCMe CH (E4°) (285° uncor). Formed from acetone and m-xylidine (Levin a Riehm, B 19, 1394) White plates (from ether)—B'H₂SO₄. (235°-242°); needles, v sol water, m. sol alcohol—B'HCl: white needles (by sublimation).—B'₂H₂PtOl₅.—B'₂H₂Cr₂O₇. orange needles, sl sol water

Tetramethylquinoline C₁₈H₁₈N (265°-278°). Occurs in crude quinaldine, obtained from par

aldehyde, aniline, and HClAq (Einhorn, B 18, On oxidation with CrO₂Cl₂ it yields an aldehyde C15H15NO, crystallising from water in needles (containing Saq), melting at 74° when hydrated and 102° when anhydrous, it is oxidised by ammoniacal AgNO, to an acid crystallising ın needles [224°

Salt -B'2H2PtOl

References - Amido-, Chloro, Nitro-, and OXY, METHYL-QUINOLINES, and METHYL-DI-QUINOLYL

(γ) METHYL-ISOQUINOLINE C, H,N ε ε C.H. CH N (256° uncor) Formed by the distillation of either of the compounds CMe₂ CO NH and CMe₂ CO NMe with zincdust (Le Blanc, B 21, 2300) solidified at -75° — $B'_{2}H_{2}PtCl$ Liquid, not [253 5° Brownish red crystals —B'C, H2(NO2), OH [195°] Slender needles

(a)-Methyl-isoquinoline $C_0H_0 < CH CH N$

One of the products got by distilling papaveroline over zinc dust (Krauss, M 11, 361 Oil Volatile with steam —B'₂H₂PtCl_e1½aq [229°] Orange yellow pp —Picrate [210°] Light yellow pp

Derivative —v Chloro methyl-isoquinoline METHYL-QUINOLINE-ACRYLIC ACID v

METHYL QUINOLYL ACRYLIC ACID

(Py 3)-METHYL-QUINOLINE (B 2) CARB-OXYLIC ACID C, H, NO, 2 e CO2H C CH C CH CH

Quinaldins p-carb CH CH C N CMe

[259°] Formed by the reaction of oxylic acid a mixture of paraldehyde, p amido benzoic acid, and HClAq (Doebner a Miller, B 17, 939) Formed also by oxidation of the corresponding dimethyl quinoline (Schunck, B 23, 2263) White needles, which may be sublimed Sol hot alcohol, v sl sol water — HA'HCl aq long slender meedles or small prisms—(HA')₂H_PtCl₄ 4aq monoclinic tables—(HA')₂H_Cr O, red needles, sol hot water—CaA'₂ 2aq feathery crystals— CuA', 6aq small plates -AgA' sparingly soluble crystalline powder — *PbA'₂ prisms
(Py 3)-Methyl-quinoline (B 3) carboxylic

CH CH C CH CH acid CO₂H C CH C N CMe Quinaldine m carboxylic acid [285°] Formed by heating a mixture of paraldehyde, m amido benzoic acid, and HClAq (Doebner a Miller, B 17, 941) Formed also by the oxidation of the corresponding aldehyde by Ag₂O (Eckhardt, B 22, 281) Formed also by oxidation of the corresponding di methyl quinoline (Rist, B 23, 2262), and from the corresponding amido methyl quinoline by Sandmeyer's reaction (Rist, B 23, 3485) Long silky needles which may be sublimed alcohol, nearly insol water - HA'HCl aq small tables, si sol cold water -(HA')2H2PtCl monoclinic prisms — (HA')₂H₂Cr₂O, yellov needles, v sol hot, sl sol cold, water — CaA', 2aq sparingly soluble prisms —CuA', 2aq green tables —AgA' crystalline pp

(Py 3)-Methyl-quinoline (B 4)-carboxylic aeid CH OH — C CH CH Quinaldine o carb-

a Miller, B 17,943) Formed also by oxidation of the corresponding di-methyl quinoline (R. Meyer, B 23, 2259) Colouriess needles (containing ½aq), v sol hot water and alcohol. Split up by heat into CO₂ and quinaldine.— HA'HCl · concentric tables, v sol water -(HA')2H2PtCle 2aq large red prisms, sol hot. sl sol cold, water — CuA', 1 aq small dark-green needles — *AgA' amorphous pp , changing into slender needles when heated with water for a long time

(B 4)-Methyl-quinoline (B 1)-carboxylic CH C(CO,H) > C,H,N o-Methyl-quinohne CH C(CH,) Prepared by acid [286°] ana-carboxylic acid Prepared by heating the corresponding di methyl-quinoline with dilute HNO, at 170° (Lellmann a Alt, A. 287, 310) White powder Yields (B 4) methyl-quinoline on distillation with lime A solution of its ammonium salt gives a dirty green pp with FeSO,, a light green pp with CuSO, and a white pp with lead acetate Salts — HA'HCl aq

silky needles - $(HA')_2H_2PtCl_6$ 6aq yellow needles — $(HA')_2H_2PtCl_6$ 2aq needles — $(HA')_2H_2PtCl_6$ — (HA'),H,PtCl, 2aq

crystalline pp (Py 3)-Methyl-quinoline (Py 1) carboxylie acid C₆H₄<N C(CO₂H) CH N CMe Antluvitoric acid. [242°]

Formation -1 By boiling a mixture of aniline and pyruvic acid with water, or by boiling anilpyruvic acid with water. In this reaction CH₃ CH CH CO CO₂H may perhaps be assumed as an intermediate acid (Bottinger, B. 14, 90, 133, A 191, 321) - 2 By oxidising (Py 1,3) di methyl quinoline with CrO, (Beyer. J pr [2] 33, 411, Seitz, B 23, 2257) heating isatin with acetone and dilute (5 pc) NaOHAq (Pfitzinger, J pr [2] 38, 582)

Properties -Lamine or needles (containing aq), sol water and alcohol, v e sol dilute

Tastes bitter acids

Reactions —1 Yields quinsldine on distillation with lime (Kusel, B 19, 2249) -2 Oxidised by KMnO₄ to pyridine tricarboxylic acid — 3 Bromine in chloroform forms an oily additionproduct, which gives up all its bromine on treatment with boiling water (Böttinger, B 16, 2357)

Salts —HA'HClaq needles, loses its HCl when treated with cold water — (HA')₂H₂PtCl₈2aq —HA'HBr 2aq --BaA'₂aq —AgA' small plates. (Py 2) Methyl quinoline (Py 3)-carboxylic

acid C₆H₄ CH CMe N C CO₂H [144°] Formed by oxidation of (Py 2, 3)-methyl ethyl-quinoline (derived from aniline and propionic aldehyde) with CrO, and H2SO, (Doebner a Miller, B 17, 1715, 18, 1641) Long silky needles or monoclinic prisms (from ether alcohol), sol hot water and alcohol Split up at 160° into CO₂ and (Py 2) methyl-quinoline —CuA', sl sol water. (Py 3)-Methyl quinoline (Py 2) carboxylic

acid C.H. CH C CO.H Quinaldine carboxyhc [2349] Formed by saponification of its ether, which is produced by the action of oamido-benzoic aldehyde on an alkaline aqueous oxylic acid [151°] Formed by heating a solution of acetoacetic ether (Friedländer a Göhmixture of o amido benzoic acid (25 g), paraldehyde (13 g), and HClAq at 100° (Doebner oxidising (Py 2, 3)-di methyl quinoline with

chromic soid (Rohde, B 22, 267) Colourless | needles, al sol water, m sol alcohol. Split up on fusion into CO, and quinaldine.

Ethyl ether EtA'. [71°] Long white needles, insol water May be distilled.— (EtA')₂H₂PtCl₄2aq sparingly soluble yellow

needles.

Methylo-rodide of the ethyl ether [205°] Orange needles, sl sol cold EtA'MeI water and alcohol, v sol hot water Ag2O con verts it into the oxide (EtA'Me),O, an amorphous pp which, when freshly prepared, is sol benzene and chloroform, insol water, alcohol, ether, and ligroin, after a time it becomes insol benzene The oxide decomposes when and chloroform heated between 180° and 240° HCl converts it into EtA'MeCl, which yields (EtA'MeCl)2PtCle, crystallising in golden plates [217°]

(Py 1) Methyl-quinoline (B 2) carboxylic CO₂H C CH C CMe CH

Lepidine p carb. HCCHC N CH oxylic acid [250°-270°] Obtained by oxidation of the corresponding di methyl quinoline by chromic acid mixture (K Daniel, B 23, 2264) Stellate groups of needles Yields lepidine on distillation with sods lime

Methyl-quinoline carboxylic acid C12HeNO2 oxidising the fraction 275°-285° (? di methyl Formed by quinoline) of the product of the action of aniline on a mixture of isobutyric aldehyde, methylal, and HCl (Von Miller a Kinkelin, B 20, 1940) Small crystals, m sol water and alcohol, gives off CO, on fusion

 $(P\bar{y}$ 4) Methyl quinoline tetrahydride (B 3)carboxylic acid

CH CH C CH, CH, CO,HC CHCNMe CH.

Kairohne m-carboxylic acid [164°] Obtained by heating quinoline tetrahydride (B 3) carboxylic acid with MeI at 150° (Fischer a Korner, B 17, 765) Needles, sl sol water, v sol alcohol.

(Py 4) Methyl quinoline tetrahydride (Py 1) carboxylic acid C₀H₄ CH(CO,H) CH₂ Methyl tetrahydro cinchonic acid Formed by

heating the hydrochloride of quinoline tetra hydride (Py 1) carboxylic acid with MeOH and MeI at 100°, and decomposing the resulting salt with Ag₂O (Weidel, M 3, 66) Crystallises from cold alcohol in large prisms (containing 2aq), sol water and alcohol, nearly insol ether Reduces warm ammoniacal AgNO₃ Decomposes on distillation, yielding an anhydride C22H24N2O3, which is a colourless oil (298° at 744 mm), insol ether, alcohol, and dilute acids, and is converted by heating with HClAq at 150° into MeCl and quinoline tetrahydride (Py 1) carboxylic acid (Weidel a Hazura, M 5,643) On heating the anhydride with aqueous KOH it is converted into 'homohydrocinchonic acid' $C_{11}H_{12}NO_{21}$, which crystallises in pearly leaflets [125°], insol water, sol alcohol and ether, and forms a hydrochloride C11H12NO2HClaq, crystallising in trimetric prisms (a bc = 931207), and a methylo-10dide $O_{11}H_{12}NO_2MeI$ aq, forming monoclinic crystals, converted by Ag_2O into $O_{11}H_{12}MeNO_2$ aq, crystallising in glittering prisms, v e sol water

Salts -The metallic salts are extremely deliquescent. — HA'HCl aq large monoclinic

orystals -(HA')2H2PtCl large orange orystals. -HA'HIaq large monoclinic crystals

(B 2, Py. 3) Di-methyl-quinoline (Py 1)carboxylic acid CMe CH C C (CO.H) CH CH CH C

[262°] Formed by the action of aqueous NaOH on a mixture of p methyl-isatin and acetone (Pfitzinger, J pr [2] 38, 584) Shining plates (from water)

(B 4, Py 8)-Dimethyl-quinoline (B 2)-carb oxylic acid

> CO.H C CH CH CH CH CMe C N CMe

Formed by oxidising (B 2, 4, Py 3) trimethylquinoline with CrO₃ and dilute H₂SO₄ (Panajo toff, B 20, 38) Needles (by sublimation), sl. sol water and cold alcohol On distillation with

lime it gives (B 4, Py 3)-di-methyl-quinoline Salts—(HA')₂H₂PtCl₈4aq orange needles. BaA'₂ white needles, v sol water —AgA'aq amorphous precipitate becoming crystalline — $C_8H_2(NO_2)_8OH$ [221°] Yellow needles, sl sol.

water, v sol alcohol

(Py 2, 3) D₁ methyl-quinoline (B. 2)-carboxylic acid CO₂H C CH C CH CMe [270°] HC CH C N CMe Formed by oxidising (B 2, Py 2, 3 tri methyl quinoline (Miller a Ohler, B 23, 2268) Silky

needles, sl sol water and alcohol Gives on distillation (Py 2, 3) di methyl quinoline [68]

-CuA'2 aq $(Py^2 \hat{\mathbf{3}})$ -Methyl-quinoline (B 2, Py 1) di carboxylic acid CO2H C CH C C(CO2H) CH CH CH C N CMe

Formed by heating p amido benzoic acid (30 g) with pyruvic acid $(\bar{2}0 g)$ and aldehyde (12 g) in alcoholic solution on a water bath (Von Miller a R Meyer, B 23, 2262) White powder, insol alcohol and other solvents Cakes together at Gives quinaldine on distillation with lime — CuA'₂ green crystalline pp (Py 3)-METHYL-QUINOLINE (B 3)-CARB

OXYLIC ALDEHYDE C,1H,NO 1 e

CH CH C CH CH [61°] Prepared by COHC CHC N CMe adding KMnO₄ to a dilute solution of sodium methyl quinolyl acrylic acid covered with benz ene and frequently shaking (Eckhardt, B 22, Slender hair like crystals (containing 12 aq!) Melts at 61° when anhydrous and 73° when hydrated V sol dilute HClAq, sl sol acetic acid, v sol alcohol, ether, and benzene, m sol ligroin and hot water Volatile with steam Reduces ammoniacal AgNO₃ Gives a crystalline sulphite, and a red colour with phenyl hydrazine acetate Ag₂O oxidises it to the corresponding carboxylic acid [285°] heating with methyl-quinoline and ZnCl, for 2 hours at 150° it yields a condensation product $[69^{\circ}]$

Salts — B'HCl B'H₂PtCl₆ [211°] pale yellow needles -Triclinic crystals (from alcohol containing HCl) - B'C, H2(NO2),OH. [182°] Needles, blackening at 174°

Phenyl-hydraside C17H15N2 The salt C17H18N3HCl separated as brick-red hair-like crystals on adding a hot solution of phenyl hydrazine hydrochloride to a hot solution of the base in HClAq In presence of H2SO, the salt (C17H18N3)4(H2SO), 9aq separates in small brick red needles

(Py. 8) Methyl-quinoline (B 2)-carboxylic CHO C CH C CH CH aldehyde [106°] CH CH C N CMe Formed by oxidising the corresponding methylquinolyl acrylic acid with KMnO4, accompanied by agitation with benzene (Miller a Kinkelin, B. 18, 3237) Needles (from water), m sol ligroin and hot water, v e sol alcohol, ether, benzene, and acids On heating with quinaldine at 150° it forms C.H.N CH CH C.H.NMe, a yellow insoluble substance melting above 800° .-B2H2PtCle 2aq orange prisms

C17H15N2. Phenyl hydraside [160°]. Golden prisms (from alcohol)

(B 2, 4) Di methyl quinoline oxylic aldehyde CMe CH C CH CH CH [107°] Formed by oxidising (B 2, 3) di methyl quinolylacrylic acid with KMnO (Panajotoff, B 28, 1471) Yellowish plates, v sol alcohol and ether, sl sol water Sol acids, insol alkalis

Tri-methyl-quinoline carboxylic aldehyde C₁₈H₁₈NO [101 5°] Formed from tetra methylquinoline (derived from paraldehyde, aniline, and HCl) by treatment with CrO₂Cl, followed by water (Einhorn, B 18, 3144) Crystallises from water in needles (containing 3aq) which melt at When anhydrous it melts at 101 5° reduces ammoniacal AgNO, forming a mirror It yields an oxim [203°] and a phenyl-hydrazide [207°]

METHYL-QUINOLINE MERCAPTAN

METHYL-QUINOLYL MERCAPTAN

2)-METHYL-QUINOLINE (B 4)-SUL-PHONIC ACID C, H, NSO, 26

C(CH₃) CH CH C(SO₃H) C₃H₃N p-Toluquinoline sulphonic acid Formed by boiling a mixture of p-toluidine sulphonic acid, nitrobenzene, glycerin, and H.SO, (Fischer a Wittmack, B 17, 441) Formed also by the sulphonation of (B 2) methylquinoline (Herzfeld, B 17, 1552) Colourless plates, sl sol boiling water -KA' v sol water -BaA', (dried at 130°) amorphous, al. sol water

(B 4) Methyl-quinoline (B 1)-sulphonic acid CH C(SO₃H) O₅H₃N Obtained by heating otoluidine sulphonic acid C.H.Me(NH.)SO.H [1 2 4] with glycerin, nitrobenzene, and H₂SO, (Herzfeld, B 17, 904) Formed also by sulphonating (B 4) methyl quinoline (Herzfeld, B 17, 1550) Flat prisms (from water), v sol water —KA' long soluble tables —BaA'2 soluble trimetric tables

 $(B\ 4)$ -Methyl-quinoline $(B\ 2)$ -sulphonic acid

SO,H C CH CHe C,H,N Formed by heating otoluidine sulphonic acid C.H.Me(NH2)SO3H [1 2 5] with glycerin, mitrobenzene, and H₂SO, (Herzfeld, B 17, 903) Colourless sparingly soluble prisms

(Py 8) Methyl-quinoline (B. 2)-sulphonic acid SO,H.O CH C CH CH Quinaldine p-CH CH C N CMe. sulphonic acid Formed in small quantity in the sulphonation of quinaldine Prepared by heating amido-benzene p-sulphonic acid (100 pts) with paraldehyde (80 pts) and HCl (100 pts.) for 2 hours on the water-bath (Doebner a Miller, B. 17, 1708) Small monoclinic crystals, v sol. hot

On fusion with KOH it yields oxywater methyl-quinoline [213°]

(Py 3) Methyl-quinoline (B. 4)-sulphonic acid CH OH — C OH CH Quinalding o-sul-phonic acid Formed, in small quantity, in sulphonating quinaldine (Doebner a. Miller, B 17. Long flat triclinic prisms, v sol. hot On fusion with potash it yields oxywater methyl quinoline [74°]

(Py. 8) Methyl-quinoline (B 1 or 8)-sul-

- CH CH Quinaldine m sul-C(SO₂H) CH C N CMe phonic acid The chief product of the sulpho nation of quinaldine (Doebner a Miller, B 17, 1703) Glistening monoclinic prisms, sol hot, sl sol cold, water On fusion with potash it gives oxy methyl quinoline [234°] Distillation with KCy yields the nitrile of the corresponding carboxylic acid (Richard, B 23, 3488)

(Py 1) Methyl-quinoline sulphonic acid C₆H₃(SO₃H)<N CH CH Lepidine sulphonic acid \mathbf{CH} Formed by heating 'homohydrocinchonic acid' $C_{10}H_2NSO_3$ with H_2SO_4 at 180° (Weidela Hazura, M 5, 652) Crystallises from water in thin plates (containing aq), nearly insol cold, v. sol. hot water

(Py 1) Methyl quinoline (B 2) sulphonie acid SO, H C CH C CMe CH Formed by heat-HC CH C N-CH ing lepidine (1 pt) with H_2SO_4 (8 pts) at 300° (Busch a Koenigs, B 23, 2680) Silky needles (containing xaq), v sol hot water -AgA' aq. white jelly, becoming crystalline

(Py 1, 3) Di-methyl-quinoline sulphonic acid C₁₁H₁₁NSO₂ s.e C₆H₃(SO₅H) < CMe CH CMe Formed by sulphonating the corresponding di methylquinoline (Beyer, J pr [2] 33, 407) Tables or flat needles, not melting below 303° On fusion with potash it yields oxy di methyl quinoline

(B 1, 4) D₁-methyl-quinoline (B 2) sulphonic acid SO₃H C CMe C₅H₃N. p-Xyloquinoline sulphonic acid Formed by heating (B 1, 4)-dimethyl-quinoline with fuming H2SO4 Formed also from xylidine sulphonic acid by heating with nitrobenzene, glycerin, and H₂SO₄ (Nölting a Fruhling, B 21, 3157)—KA' needles or plates, v. sol water—BaA's aq plates, v sol. hot water -BaA'2 2aq

(B 1, 4)-Di-methyl-quinoline (B. 8)-sulphonic acid SO₂H C CMe CMe C₅H₂N Formed by heating xylidine sulphonic soid (derived from p xylene sulphonic acid) with nitrobenzene, glycerin, and H.SO. (Nölting a Frühling, B 21, Short white plates, sl sol cold water, v. sol hot water and dilute acetic acid —KA'aq e sol. water -BaA', aq. needles, v. sol. hot

(B 2, 4)-D1-methyl-quinoline sulphonic soid C.HMe. (SO, H) (C.H.N) Formed by heating the corresponding di-methyl-quinoline with fuming H.SO, at 165° (Berend, B 17, 2716). Minute needles (from alcohol-ligroin).

(B 2, 4, Py 3)-Tri-methyl-quinoline (B 1)sulphonic acid. Formed from the corresponding tri-methyl-quinoline by heating with H2S2O, at 125° (Panajotoff, B 20, 36) Small yellow needles (from dilute HClAq), not melting at 260°. insol cold water —BaA', Saq silky needles
METHYL-QUINOLINIC ACID v METHYL-

PYRIDINE DICARROXYLIC ACID

METHYL-QUINOLINIUM HYDRATE

Methylo-hydrate of Quinoline (Py 1)-METHYL-(Py 3 B 8)-DIQUINOLYL

CMe CH CH CH • NCH

[188°]. Obtained by heating flavaniline (10 pts), with nitrobenzene (5 pts), glycerin (30 pts), ind H₂SO₂ (80 pts.) (Fischer, B 19, 1036) Jolourless crystals Strong base Its salts Its salts with mineral acids have a splendid blue fluorscence in dilute solution

Methylo-sodide B'MeI fine yellowish

seedles, easily soluble in water

Di-(Py 3) methyl-diquinolyl C₂₀H₁₆N₂ v e $\stackrel{?}{H} \stackrel{.OH}{\sim} C_{\bullet}H_{\bullet} C_{\bullet}H_{\circ} \stackrel{CH}{\sim} \stackrel{CH}{\sim} \stackrel{CH}{\sim} [207^{\circ}]$ (above Prepared by gradually adding paraldehyde (90g) to a solution of benzidine (80g) in sone HClAq (400 g) at 100° After heating for ien hours the product is diluted with water, reated with NaNO2, boiled, and ppd by KOH Hinz, A 242, 326) Slender white needles, sol sloohol, benzene, and chloroform, sl sol water and ether.—B"H2PtCl, 2aq light yellow pp, al iol. hot water -B"2HNO3 small colourless needles, v sol water, sl sol alcohol -B"H2Cr2O, slender yellow needles, al sol hot water

Di-methyl diquinolyl C20H16N2 aq Formed by heating quinaldine with sulphur (Von Miller, B 21, 1828) Crystallises from alcohol in white needles (containing aq) picrate crystallises in needles The platinochloride forms needles, v sl sol water

Tetra-methyl-diquinolyl C22H20N2 2.6 CH CMe N C_eH_1 C_eH_3 CMe CH CMe

Tetra-methyl diquinolyline [232°] Formed by heating benzidine with acetone and conc HClAq at 180° (Schestopal, B 20, 2506) White plates, msol water, sl sol ether, v sol alcohol When heated with benzoic aldehyde and ZnCl. at 180° it forms a compound crystallising from alcohol in yellow needles

Salts—B"H₂Cl₂. Needles, v sol water and ohol—B"H₂SO₄ Needles (from water) or alcohol -B"H2SO, prisms (from alcohol) -B"H2PtCl needles B"H2Cr2O, needles, sl sol cold water -P1insol water and cold alcohol. -

B"LCl, 2HCl flesh coloured needles

Methylo-rodide B"Me,I, [270°]. Ethylo-rodide B"Et,I, [158°] Ethylo-rodide B"Et.L. [158°] (Py 3)-METHYL QUINOLYL-(B 2)-ACRY-CO'H CH CH C CH C CH CH

CH.CH C N CMe

Quanaldine-acrylic acid Obtained by heating a mixture of paraldehyde(40g), p-amido-cinnamicacid hydrochloride (50 g.), and conc. HCl (50 g) (Miller a. Kinkelin, B 18, 3235) Small concentric needles Decomposes between 240° and 250° Sol hot alcohol, sl sol. cold alcohol and water. By an alkaline solution of KMnO, it is

oxidised to methyl-quinoline carboxylic aldehyde C,H,Me CHO

Salts -A'H,HCl aq easily soluble concen trie prisms — A'Ĥ, HNO, aq needles or prisms, sl sol dilute HNO, — (A'H, HCl), PtCl, 2aq, reddish-yellow prisms

(Py 3)-Methyl-quinolyl (B 3)-acrylic acid он сносносн C12H11NO2 2 6. CO2H CH CH C CH C N CMe [246°] Obtained by heating m-amido-cinna mic acid with paraldehyde and conc HClAq at 150° (Eckhardt, B 22, 272) Small white monoclinic prisms (from alcohol), tending to become yellow, sl sol ether, chloroform, and petroleum ether, m sol alcohol, benzene, and When heated above its melting point acetone a small sublimate of slender needles [223°] is obtained. KMnO₄ oxidises it to the correspond ing methyl-quinoline carboxylic aldehyde warming with chloral on the water bath two compounds are formed One of these compounds C1.H8NO2.CH2 CH(OH)COls crystallises from alcohol in prisms [201°], which dissolve in nitric acid with violet fluorescence, and which yield the salts $C_{15}H_{12}Cl_1NO_3HCl$ [over 300°] and AgC, H, Cl, NO, crystallising in slender needles The other compound C28H25Cl5N2O5 crystallises from alcohol in needles [128°] which dissolve in nitric acid with blue fluorescence, and which forms a salt C₂₈H₂₅Cl₅N₂O₅HCl [217°]

Salts -HA'HClaq deliquescent trimetric needles — (HA')₂H₂PtCl₈ 2aq yellow needles or plates — HA'HNO₃ aq needles, sol water — HA'C,H2(NO2)OH aq [152°] Bundles of slender needles, sol alcohol, hot water, and HOAc, sl sol ether —CaA'₂ 3aq slender needles (from water), v sol dilute HClAq and acetic acid -AgA'2aq minute crystalline lancelets -

AgA'4aq needles

(Py 3)-Methyl-quinolyl-(B 1?)-acrylic acid C, H, NO. Formed on one occasion in the preparation of the preceding isomeride (E) Crystallises in yellowish monoclinic plates (con taining aq) [184°] and in white crystals (containing & ÉtOH) [204°] Its ammoniacal solu tion, unlike that of its isomeride, is not ppd. by salts of Ba, Ca, and Mg

(B 2, 4)-D₁-methyl-(Py 8)-quinolyl-acrylic acid CMe CH C CH CH CH CH CH CO2H Formed by boiling the compound of chloral and (B 2, 4, Py 3) tri-methyl-quinoline with aqueous K CO, (Panajotoff, B 20, 42) Yellowish needles, de composing at 180°, forming a product melting at 210°

METHYL-QUINOLYL-AMMONIUM IODIDE v. Methylo-rodide of Quinoline

(Py 1)-METHYL-QUINOLYL ETHYL SUL-PHIDE C.H. CMe CH Formed by treating methyl-quinolyl mercaptan with NaOEt and EtI (Roos, B 21, 628) Oil, volatile with steam H2PtOl. aq —B'HI [214°] Long yellow -R needles

(Py 3)-Methyl-quinolyl ethyl sulphide C.H. CKEt) CH [56°]. Formed from sodium methyl-quinolyl mercaptide and EtI (R). White needles, v. sol. alcohol and ether, insol. TETRA - METHYL - DIQUINOLYLINE
TETRA METHYL DIQUINOLYL.

(Py 1) METHYL (Py 8)-QUINOLYL MER.

CAPTAN C.H. CMe CH [258°] Formed

by heating (Py 3, 1) oxy methyl quinoline with P_2S_3 at 150° , extracting the product with HClAq and ppg with water (Roos, B 21, 625) Brownish needles (from alcohol), insol water, sl sol cold alcohol, v. sol ether Not attacked by hydroxylamine or phenyl-hydrazine H_2O_2 oxi dises it to a disulphide NaOEt and EtI form methyl quinolyl ethyl sulphide

[167°] Prepared by axidising the corresponding mercaptan with hydrogen peroxide (Roos, B 21, 627) White plates (from benzene), v sol alcohol, ether, and benzene, insol water and alkalis

(Py 3) - METHYL - (B 4) - QUINOLYL PHENYL KETONE C_1, H_1, NO i e

CH CH CH CH CH (B 4)-Benzoyl-quinaldine [108°] Colourless felted needles Formed by boiling o amido benzophenone (1 pt) and par aldehyde (2 pts) with dilute H₂SO₄ (15 pts) (Geigy a Koenigs, B 18, 2406)

(Py 3)-methyl-(B 2)-quinolyl phenyl ketone C₆H₅CO C CH C CH CH CH [68°] (above

OH CHCN CMe [103] (above 300°) Formed by adding paraldehyde (1 mol) in conc HClAq and digesting the mixture on a water bath (Hinz, A 242, 323) Plates (from alcohol), v sol hot water, alcohol, and ether — By'H_PtCl₈ 2aq needles Melts at 110° when anhydrous —B' H Cr.O, needles

Methylo-10dide B'MeI [220°]

(B 2)-METHYL-QUINOXALINE C,H,N, te СМ, СН С И СН Toluquinoxaline (244° un-CH CHCNCH Obtained by the action of glyoxal on (1, 3, 4) tolylene diamine, and purified by means of its compound with NaHSO, (Hinsberg, B 17, 321, A 237, 336) Liquid, turning yellow in air and light, miscible with cold water, alcohol, ether, and benzene, less soluble in hot water With tin and HClAq it gives a blue colouring matter Forms a dibromide C, H, Br, N, crystallising from chloroform in needles, which blacken and decompose at 170° -B'2H2PtCl vellow needles, al sol water and alcohol -B'2H2C2O4. Needles [136°], sl sol water

Compound with sodium bisulphite B'(NaHSO₃), 2aq slender needles; v. sol water,

m sol alcohol

Ethylo-rodide B'Etl. Colourless crystals, v. sol. water, sol alcohol and chloroform

Derivatives - V CHLOBO TOLUQUINOXALINE

(B 2, Qu 2) - Di - methyl - quinoxaline CMe CH CN CH CH CH CN CMe · 'Methyl tolylene-quinoxalme' [54°] (268° uncor). Formed by the action of chloro-acetone (2 mols) on an aqueous solution of (1, 3, 4) tolylene diamine (Hinsberg, B 19, 485, A 237, 368) Formed also by the action of tolylene o diamine upon methyl glyoxal or its oxim, nitroso acetone (Pechmann, B 20. 2544) White crystals, turning red in the air, v e sol cold water, alcohol, and ether Ppd from its aqueous solution on boiling or on adding KOH Not affected by nitrous acid or Ac₂O -B'2H2PtCl, yellow needles al sol water

Tri methyl-quinoxaline CMe CH C N CMe (91°) (271°) Formed by the action of dimethyl diketone (diacetyl) on (1, 3, 4) tolylene diamine acetate (Pechmann, B 21, 1414) Hexa gonal crystals (from hgroin)

Tetra-methyl diquinoxaline, so called,

CMe N C CH C N CMe
CMe N C CH C N CMe
by warming tetra amido benzene with excess of
di methyl diketone CH, CO CO CH, (Nietzki a
Muller, B 22, 444) Reddish star shaped plates
(from aniline) Nearly insol water, alcohol, and
ether Its solution in cone H SO, is bluish
green, and becomes blue on dilution

METHYL-QUINOXALINE DICARBOXYLIC ACID C₁₁H₈N₂O₄ 16 CMe CH C N C CO₂H CH CH C N C CO₂H Toluquinoxaline dicarboxylic acid Prepared by the action of an aqueous solution of (1, 3, 4) tolylene diamine on sodium di-oxy tartrate (carboxytartronate) at 80° (Hinsberg, A 237, 353) Colourless needles or prisms, v sol water, v sl sol benzene When crystallised from water its molecule contains ½ aq The anhydrous acid de composes at 130° into CO₂ and a mono carboxyliq acid SnCl₂ forms a compound crystallising in dark green needles, sl sol water

METHYL-QUINOXYL v (Py 1)-OXY-METHYL

METHYL-RESORCIN v ORCIN

Di-methyl-resorcin v Di methyl derwative of Resorcin

Tr1 - methyl - resorcin C₆H(CH₃)₃(OH)₃ [1 3 5 2 6] Dr oxy mesitylene Mesorcin [150°] (275° cor)

Preparation —Nitro mesidine, obtained by partial reduction of di-nitro mesitylene, is treated with HNO₂ and converted into intro mesitol, by reduction of this and treatment again with HNO₂ mesoroin is obtained (Knecht, B 15, 1375)

Properties — White plates sl sol cold water May be sublimed Reduces ammoniacal AgNO, in the cold By Fe₂Cl, it is oxidised to oxy isoxyloquinone Heated with H₂SO₄ it gives a substance whose alkaline solution is pink with an intense green fluorescence

Dr-acetyl derivative C,H₁₀(OAc)₂ [63°] (805° cor)

METHYL ROSANILINES v METHYL-TRI
AMIDO DI PHENYL-TOLYL-CARBINOLS

Methyl - pararosanilines v Methyl - TRI

DI-METHYL - ROSINDOLE $C_{2}H_{20}N_{2}$ *.e $C_{6}H_{5}C < C_{6}H_{5}N$ (?) • [o 270°] Formed

together with benzoyl methyl-indole by heating methyl-indole (methyl ketole) with benzoyl chloride and ZnOl. Also formed by oxidation of the leuco-compound benzylidene-methyl-indole Amorphous yellow pp, v sol alcohol and ether, or yellowish-red prismatic crystals, sl sol alcohol, ▼ sl. sol ether. The amorphous modification is converted into the crystalline by long boiling with water It dissolves in acids and in alcoholic NaOH or KOH with a red colour Its salts are red dyestuffs closely resembling resamiline minc-dust and NH, it is reduced to benzylidenemethyl indole [248°]—B'HCl small metallic green crystals, al sol water (Fischer a Wagner, B 20, 815)

METHYL SALICYLIC ACID v Oxy-TOLUIC ACID and the Methyl derivative of o-OXY BENZOIC

METHYL-SALICYLIC ALDEHYDE v Methyl derivative of o OXY BENZOIC ALDEHYDE

DI-METHYL-SELENAZOLE v SELENIUM, ORGANIC COMPOUNDS

METHYL-SELENIDE & SELENIUM, ORGANIC

COMPOUNDS

METHYL SILICATE C₄H₁₂S₁O₄ t e S₁(OMe)₄ (2°) S G 2 10589 V D 538 (calc 526) (122°) SG 2 10589 VD 538 (calc 526) Formed by the action of SiCl, on dry methyl alcohol (Friedel a Crafts, A Ch [4] 9, 32) Colourless liquid with fragrant ethereal odour, m sol water, the solution depositing gelatinous silica when kept for a month When heated with SiCl, in various proportions it gives rise to the SiOl, in various proportions it gives rise to the compounds ClSi(OMe), (115°), S G 2 1 195, V D 5 58 (calc 5 42), Cl₂Si(OMe)₂, (c 100°), S G 2 1 260, V D 5 66 (calc 5 57), and Cl₂Si(OMe), (c 84°), V D 5 66 (calc 5 79)

Hexa-methyl disilicate Me₆Si₂O, (202°)

S G 2 1144 V D 9 19 (calc 8 98) Formed

when, in the preparation of Me,SiO, the methyl alcohol is not quite dry Formed also by heating Me,SiO, (2 mols) with water (1 mol) and methyl alcohol

METHYL-STIBINE v Antimony, Compounds with organic radicles, vol 1 298

METHYL - STILBAZOL O STYRYL METHYL-PYRIDINE.

METHYL-STILBENE v. s-PHENYL-TOLYL-BTHYLENE

Di-methyl-stilbene v Di-Tolyl-ETHYLENE Tetra-methyl-stilbene v DI-XYLYL-ETHYLENE METHYL-STRYCHNINE & STRYCHNINE METHYL-STYRENE & TOLYL-ACETYLENE

METHYL STYRYL KETONE v. STYRYL METHYL KETONE

METHYL-SUCCINIC ACID & PYROTARTABIO

C.H.O. 1. Isobuu-Di-methyl-succinic acid CO.H CH. CMe. CO.H Isoadvprc acid tane dicarboxylic acid Mol w. 146 [140°] HCv 671,400 HCp 671,700 H.F 237,300 (Stohmann, Kleber, a. Langbein, J pr [2] 40, 212)

Formation.-1 From its imide, which is formed, together with di-methyl malonamic acid, by oxidising mesitylic acid C_sH_{1s}NO, with KMnO₄ in acid solution (Pinner, B 15, 582) — 2 By boiling with HClAq the isobutane tricarboxylic ether OO_Et OMe_CH(CO_Et), obtained by the action of a-bromo isobutyric ether on sodio malonic ether (Leuckart, B 18, 2350, Bischoff, B 28, 1948). Formed also by heating

the corresponding isobutane tricarboxylic acid (Barnstein, A 242, 133) -8 By oxidising with chromic acid mixture the terpene C20 H22 obtained from copaiva balsam (Levy a Englander, A 242, 192)—4 By oxidising tropilene C,H, with nitric acid (S G 138) (Ladenburg, A 217, 139)—5 By heating its nitrile (obtained from isobutylene bromide and KCy) with HClAq at 150° (Hell a Rothberg, B 22, 1740) Properties —Thick colourless prisms (from

benzene), crystallising from water in efflorescent monoclinic forms, a b c = 2029 1 1 191; $a = 118^{\circ} 36'$, $\beta = 95^{\circ} 16'$, $\gamma = 101^{\circ} V$ sol water, alcohol, ether, and acetone, v sl sol chloroform and ligroin At about 185° it splits up into CO₂

and its anhydride

Salts — KHA" 2 aq small KHA" 5 aq (B) — NaHA" 3 aq small prisms (P) prisms, $\vec{a} \ \vec{b} \ \vec{c} = 1 \ 8365 \ 1 \ 4 \ 1801$, $\beta = 90^{\circ} \ 43'$ (L a E)—Na,A"11aq needles, v sol water—
NH,HA"—(NH,)2A"—BaA" 2aq (B)—
BaA" 2½aq monoclinic plates, a b c=1 601. 11790° , $\beta = 97^{\circ} 26'$ Sl sol hot, m sol cold, water, insol alcohol (L a E) — CaA" aq minute plates, sl sol water, insol alcohol — —CdA" 6aq — CuA" 2aq — PbA" aq — Ag,A": white pp, v al sol water

Methyl ether Me2A" (200°) 1 0568

Ethyl ether Et.A". (215°) SG 17 1 0134 (B), 17 9976 (L a E)

Anhydride CMe, COOO [29°] (B), (220°) (L a E)

 $\dot{O}hloride_{C_2H_2Me_2(C_2O_2Cl_2)}$ (201°) (B), (193°) (L a E) Formed by heating the acid with PCl_s at 125° Reacts with phenyl hydraz ide, forming the compound $_{\mathrm{CH_{2}}}^{\mathrm{CMe_{2}}}$ CO N NHPh [132°], which yields a nitrosamine [76°]

Imide CMerCO NH [106°] from the chloride and NH. Plates (from ether) Yields C.H.KNO, 21aq, crystallising in prisms, v. sol alcohol

Natrale CN CH2 CMe2 CN **Iso**butylene cyanide (219°) Formed by leaving a mixture of isobutylene bromide and alcoholic KCy to stand for two weeks, heating to 140° to expel alcohol, and extracting the residue with ether (Hell a Rothberg, B 22, 1740) Clear liquid, v sol water

Anti-s-di-methyl succinic acid CoH10O4 se. CO,H CHMe CHMe CO,H Maleinoid drmethyl successic acid Butane dicarboxylic acid [120°] (O a R, H a R, B a. V), [124°] (Z) S 30 at 14°

Formation -1 Together with the isomerie 'para' or fumaroid acid [194°] by reduction of di-methyl maleïc acid (Otto a. Rossing, B 20, 2736) -2 Together with the isomeric acid [194°] by heating with HClAq the mixture of their ethers obtained by adding a-bromo-propionic ether to an alcoholic solution of a cyano propionic ether and NaOEt (Zelinsky, B 21, 8160)—8 A mixture of the ethers of the two isomeric s-di-methylsuccinic acids is also formed, with other bodies, when a-bromo-propionic ether is heated with finely-divided silver (Hell a Rothberg, B 22, 60) -4 The mixture of 'anti-' and 'para' dimethyl succinic acids is also formed by hydrolysis of butane tricarboxylic acid derived from sodium methyl malonic ether and a bromo propionic ether (Leuckart, B 18, 2346, Bischoff a Voit, B 22, 389) —5 From its anhydride, which is formed, together with the anhydride of the fumaroid isomeride, by heating the fumaroid acid [194°] for several hours at 200° (Bischoff a Voit, B 23, 641)

Properties — Concentrically grouped prismatic needles, more sol hot than cold water, v sol ether, alcohol, acetone, and chloroform, sl sol CS₂ and benzene, almost insol ligroin. A neutral solution of its ammonium salt gives a yellowish red pp with FeCl,, a greenish blue pp with cupric sulphate, but no pp with salts of Ba, Zn, Mg, Co, and Ni. Bromine at 130° con verts it into di methyl maleic acid [95°]

Salts—CaA"2aq crystalline powder, sl sol cold water—BaA"3aq thin plates, sl sol water—Ag.A" white crystalline pp

Methylether Me.A" (200°) From Ag.A" and MeI at 100° Oil, with pleasant odour

(Zelinsky a Krapivin, B 22, 646)

Ethylether Et.A" (222°) SG 2 10218, 18 10072 (Z a K), 15 10315 (B a V) H C 1,296,860 (Ossipoff, C R 109, 224) Oil, decomposed by heat into the anhydride and Et.O

Chloride (186°-197°)

Imide CHMe CO NH [106°] (B a V). [110°] (Z a K) Obtained by distilling the dry ammonium salt in gaseous NH₃ Stellate groups of prisms (from dilute alcohol) or thin needles (from benzene), v sol water, alcohol, benzene and chloroform, sl sol ether, v sl sol ligroin reconverted into the acid [120°] by alkalis

Anrilde CONHPh CHMe CHMe CONHPh [222°] Formed from the chloride and aniline

Needles (from alcohol)

Phenyl-imide CHMe CO NPh [146°] Formed by heating the acid (1 mol) with aniline (2 mols) till the amiline begins to distil Slender needles, v sol alcohol, ether, and benz ene, sl sol water

Anhydride CHMe CO [87°] When formed by heating the 'anti' acid to 200°, it yields only the 'anti' acid again when heated with water, but when formed from the 'para' acid by like treatment the product (a mixture of anhydrides?) yields a mixture of 'para' and 'anti' acids, the amount of the latter increasing with the duration of the heating Formed also from the 'anti' acid by heating with AcCl In all cases it melts at 87° When heated with bromine in chloroform at 90° it yields di methylmaleic acid

'Para' s-di-methyl-succinic acid C_eH₁₀O₄ te MeCH(CO₂H) CHMeCO₂H Fumaroid variety of s di methyl succinic acid Isoadipic acid Hydropyrocinchonic acid [194°] (O a B), (B a V) (192°) (Z) HF 238,000 HC v 670,700 HC p 671,000 (Stohmann, Kleber, a Langbein, J pr [2140, 212) S 1 at 22°

Langbein, J pr [2140, 212) S 1 at 22°
Formation—1 By heating a bromo proponic acid with reduced silver at 155° (Wishens, B 2, 720, cf anti-dimetrial succinic Acid, Formation 3)—2 By boiling (aß) dimethyl-acetyl succinic ether with conc alcoholic KOH (Hardtmuth, A 192, 143)—8 By

bolling an aqueous solution of sodium di-methyl-maleate with sodium amalgam (Weidel, A 173, 109, M 3, 612)—4 From its amide which is formed by the action of NH₄ on an oily product of the action of bromine on a solution of cyanochine in dilute H₂SO₄ (E von Meyer, I pr [2] 26, 358)—5 Together with the isomeride [120°] by the reduction of di methyl maleic anhydride by HIAq at 220° or by sodium amalgam (Otto a Beckurts, B 18, 838, Otto a Rössing, B 20, 2736)—6 By heating cyano-di methyl succinic acid with HClaq (Zelinsky, B 21, 3166)—7 Together with the 'anti' isomeride, by all the modes of formation described above for that acid—8 By heating the 'anti' isomeride for several hours with cone HClAq at 180°-190° (Bischoff a Voit, B 23, 643)

Properties—Small triclinic needles (from alcohol), si sol water, m sol alcohol On heating at 200° it yields a mixture of its anhydride and that of the 'anti' acid, after several hours' heating it is almost wholly converted into the anhydride of the 'anti' acid its neutral solution is ppd by FeCl₂, CuSO₄, BaCl₂, and lead acetate On treatment with bromine it yields di methyl-

maleic acid

Salts—NH,HA" (dried at 100°). Monoclinic prisms, v sol water—CaA" 2aq prisms (Bischoff a Rach, A 234,76)—CaA" aq (Z)—CaA" 1½aq (W) Monoclinic needles—SrA"—BaA" 4aq—PbA"—PbA"½aq short prisms—CuA"—Ag₂A"

Methyl ether Me, A" (199°) Oil (Zelinsky a Krapivin, B 22, 650) Yields the acid

[192°] on saponification

Ethyl ether Et.A" (220°) SG § 1013, 13 1002 HC 1,803,570 Oil, with pleasant odour Yields on saponification a mixture of the acids [120°] and [192°]

Chloride (186°-197°)

Imide MeCH — CO NH [78°] From the ether and NH, Crystallises from benzene

Yields only the 'para' acid on saponification Anilide McCH(CONHPh) CHMC CONHPh [235°] From the chloride and aniline Needles, sol ether and HOAc Yields only the 'para'

acid on saponification

Phenyl imids MeCH CO NPh

[126°] Formed by heating the acid with aniline Caustic potash converts it into a mixture of 'anti' and 'para' acids

Anhydride MeCH CO O [88°]

Formed from the acid and AcCl May be reconverted into the original acid. By heating the 'para' acid to 180°-196° a mixture of anhydrides [87°] is formed, which yields on saponification a mixture of 'anti' and 'para' acids

Derivative —v Di-chloro-di-methyl succinic acid

Tri-methyl-succinic acid $C_1H_{12}O_4$ a.e. CO_2H CHMe CMe. CO_2H [105°] Electrical conductivity Bischoff, B 28, 1466 Formed by the hydrolising action of H_2SO_4 on pentane tricarboxylic ether obtained from sodium methylmalonic ether and a bromo isobutyric ether (Bischoff a Mintz, B 23, 649) Yields an an hydride melting between 67° and 82°

This acid is probably identical with s-di-

methyl-glutaric acid (Bischoff a Jannsnicker, B.]

Tetra-methyl-succinic acid C.H.O. CO₂H CMe₂ CMe₂ CO₂H Hexane dicarboxylic acid Mol w 174 [192°] Formed, together with the isomeric tri-methyl-glutaric acid [97°], by heating α-bromo isobutyric ether (3 pts) with dry silver powder (2 pts) at 125° for 8 hours The product is fractionally distilled, and the fraction 200°-250° saponified by heating with HBrAq at 100° The resulting acids may be separated by steam distillation, tetra methylsuccinic acid alone passing over (Hell, B 7, 320, 10, 2229, Auwers a V Meyer, B 22, 2014, 3005, 23, 299)

Properties -- Short branching crystals, melting at 200° when quickly heated, and 192° when slowly heated, sl sol cold water, m sol hot water, ether, chloroform, and CS2, v sol alcohol

and benzene, almost insol ligroin

Anhydride [147°] (230 5°) Formed by heating the acid alone, with HClAq at 200°, or with AcCl at 100° Formed also by treating the acid (6 g) with red phosphorus (8 g) and bromine (16 g) Slender needles (from ligroin) May be sublimed Soon becomes resinous Nearly insol cold water and cold Na₂CO₃Aq, slowly dissolved by these liquids on heating, being converted into the acid

DI-METHYL-SUCCINIMIDINE C.H., N. 20

CH₂ C NH . The hydrochloride of this base

is formed by the action of methylamine on suc cinimido-ether - B'HCl glistening prisms, [248°], v sol. water, sl sol alcohol (Pinner, B

16, 1658)

METHYL-SUCCINURIC ACID Amade NH, CO NMe CO CH, CH, CONH, (?) [205°-Formed from methyl succinyl-urea CO NMe CO CH₂ and alcoholic NH₂ at 100° (Menschutkin, A 178, 210) Plates, v sl sol

DI-METHYL-SULPHAMIC ACID C2H,NSO, • e NMe₂ SO₂ OH [165°] Formed, together with hydrogen di methyl ammonium sulphate NMe₂H₂O SO₂OH, by boiling its chloride with water (Behrend, B 15, 1610, A 222, 130) Large six sided plates (from alcohol), v sol water, m sol alcohol, sl sol ether By boiling with water, alkalis, or dilute nitric acid, it is converted into

(NMe,H₂)SO,H It expels CO₂ from carbonates Salts—BaA'₂ aq plates, v sol water— PbA'₂ aq—AgA' aq v e sol water, ppd by

adding ether to its alcoholic solution Ethyl ether EtA' From the chloride and

Oil NaOEt

Chloride NMe2 SO2Cl (183° at 760 mm, 114° at 75 mm) Formed by heating dimethylamine hydrochloride (1 mol) with SO2Cl2 (13 mols) on the water-bath, the yield being 50 p c of the theoretical The product is mixed with water, and the chloride extracted with ether, shaken with aqueous Na₂CO₃, dried over CaCl₂, and distilled (Behrend) Golden yellow oil, partially decomposing on distillation with evolution of HCl V sol alcohol, ether, benzene, and shloroform, insol water, HClAq, and KOHAq

Boiling water decomposes it into HCl, H.SO. NMe₂ SO₂OH, and dimethylamine amalgam reduces it to H2S, dimethylamine, and H₂SO₄ Tin and HClAq act in like manner Zinc dust yields tetra methyl sulphamide

Amide v Di methyl sulphamide

Dimethylamide v Tetra methyl sul-PHAMIDE

Di-ethyl-amide NMe₂ SO, NEt₂ (229°) From the chloride and NEt₂H Oil, partially de composed on distillation

u-DI-METHYL-SULPHAMIDE

NMe₂ SO₂ NH₂ [96°] Formed by passing NH₃ into the chloride of di methyl sulphamic acid (Behrend, B 15, 1611, A 222, 126) Six sided prisms with pyramidal ends, v sol water and alcohol, m sol ether

s D1 methyl-sulphamide NHMe SO2 NHMe [78°] Prepared by the action of methylamine on SO₂Cl₂ in ethereal solution at 0° (Franchi mont, R T C 3, 418) Prisms, v e sol water and alcohol, v sl sol benzene Tastes sweet and alcohol, v sl sol benzene Nitric acid converts it into SO (NMe NO2)2

Tetra methyl sulphamide SO (NMe₂)₂ [73°] Formed from SO₂Cl₂ and NHMe₂ dissolved in chloroform (Behrend, B 14, 722, A 222, 119) Formed also from NMe₂ SO₂Cl and NHMe Colourless plates (from alcohol), v sol alcohol and ether, v sl sol water, aqueous acids and alkalıs May be sublimed Dry HCl at 120 decomposes it into NMe, SO₂Cl and NHMe Conc HNO₃ yields NMe₂NO₂ (Franchimont, R T C 3, 420)

METHYL SULPHATES Mono-methyl sul phate CH,OSO,OH Methyl sulphuric acid Formed by mixing methyl alcohol (1 pt) with H₂SO₄ (2 pts), allowing the hot mixture to cool, diluting with water, adding BaCO, filtering and evaporating The barium salt thus obtained is then decomposed by H_0SO_4 (Dumas a Peligot, A Ch [2] 58, 54, 61, 199, A 15, 40, Kane, P M 7, 397) Formed also from Cl SO OH and methyl alcohol (Claesson, J pr [2] 19, 240) Liquid, not solidified at -30° , v e sol water, m sol alco hol, miscible with dry ether Yields Me₂SO₄ and H2SO4 on distillation When the potassium salt is heated with potassium acetate methyl acetate is formed, methyl ethers of other acids are formed in like manner

Salts—KMeSO, aq very deliquescent mo noclinic tables, a b c = 742 779 1, β = 86° 51′ (Schabus, J 1854, 552) —Ca(MeSO₄)₂ very deliquescent octahedra —Ba(MèSO), 2 aq monoclinic tables, abc = 82419071, $\beta = 83°30'$ SG 192 2 273 —Pb(MeSO₄)₂ aq long deliquescent prisms, v sol water —UrO₂(MeSO₄)₂ aq. very deliquescent crystals (Péligot, A 56, 231)

(132 5°) at 722 mm Chloride MeO SO₂Cl Formed from SO₂Cl₂(1 mol) and MeOH (1 mol) (Behrend, J pr [2] 15, 32) Formed also from MeOCl and SO₂ (Sandmeyer, B 19, 861) Pun gent oil, decomposed by water into HCl and MeO SO₂.OH

Di-methyl sulphate Me₂SO₄. Mol w 126

(188°) S G 22 1 324 (D a P)

Formation —1 From Me₂O and SO₂ —2 By
dry distillation of MeHSO₄ (Dumas a Péligot, Claesson, J pr [2] 19, 244, B 13, 1699) -3. By distilling methyl alcohol (1 pt) with cone H_2SO_4 (9 pts), washing the distillate with water, drying the oily layer with CaCl₂, and rectifying (Dumas a Péligot, A Ch [2] 58, 32)

Properties —Oil, decomposed by boiling water and by alkalis into MeOH and H₂SO₄. An ethereal solution of NH₂ forms MeO SO₂ ONH₃Me Distillation with fused NaCl forms MeCl and Na2SO4 Distillation with KOBz yields MeOBz and K2SO4 Sodium formate yields methyl formate and so dium sulphate It forms double compounds with sulpho acetates, sulpho benzoates, and isethion-

ates (Geuther, A 218, 288)

METHYL SULPHIDE (CH₃)₂S Mol w 62 (41°) (R), (37°) (K) SG 22° 845 H.Fp 12,730 HFv 11,570 SV 756 (Lossen, A 254, 71) Formed by passing McCl into a solution of K2S in MeOH (Regnault, A Ch [2] 71, 391, A 34, 26) Prepared by distilling a concentrated solution of MeNaSO, (from 500 c c MeOH) with aqueous KOH (500 g) that has been previously half saturated with H_2S , the yield being moderate (150 g) Colourless mobile liquid with very unpleasant odour (Klason, B 20, 3407)

Reactions -1 Takes fire when dropped into dry chlorine, but if the temperature be kept low oily substitution products (CH₂Cl)₂S, (CHCl₂)₂S, and (CCl₃)₂S may be obtained (Riche, A Ch [3] 43, 283) The compound (CCl₃)₂S boiled at 156°-160° and gave a V D 568 (calc 941) -2 Iodoacetic ether forms S(CH,CO,Et), tri methyl-sulphine iodide, and Me,S(CH,CO,Et), (Letts, Tr E 28, 618) -3 Bromo acetic ether forms Me SBr CH2.CO Et which crystallises in pearly scales and yields when treated with moist Ag₂O

unstable Me,S(OH) CH, CO,Et (Letts)
Combinations—Me,SBr, Crystals (Ca
hours, A 135, 355) When dissolved in water hours, A 135, 355) When dissolved in mark training off HBr When its alcoholic solution is treated with zinc and the product evaporated and mixed with HgCl2, there is formed a pp of $(SMe_2)_2HgCl_2ZnBr_2$ (Patein, Bl [2] 50, 201) Me₂Sl₂ Crystals resembling iodine —Me SHgCl₂ —(Me₂S)₂PtCl₄ (Loir, A 107, 234) Yellow crystalline powder Melts with decomposition at 218° (Blomstrand, J pr [2] 38, 365) — (Me₂S) PtCl₂ [159°] Formed by the action of Me₂S on potassium platinum chloride at 60° (Blomstrand, J pr [2] 38, 358) Exists in two allotropic forms, crystallising in lemon yellow monoclinic crystals, and in yellow dimetric plates (containing CHCl₃) —(Me.S)(Et₂S)PtCl₂ Formed from (Et.S),PtCl and Me2S - (Me2S),PtCl2Br2. (Me2S), PtBr, reddish brown monoclinic crystals (from chloroform) — (Me,S)₂PtBr₂ Formed from (Me₂S)₂PtSO₄ and KBr (B) Yellow monoclinic crystals — (Me₂S)₂PtI₂Cl₂ greenish black crystalline powder — (Me₂S)₂PtI₂Br₂ — (Me₂S)₂PtI₄ black crystalline powder — (Me₂S)₂PtI₂ [172°] Formed from (Me₂S)₂Pt(NO₂)₂ and KI (B) Red orystals — (Me,S),Pt(NO_s), [15 from (Me₂S),PtCl₂ and AgNO_s $[156^{\circ}]$ Formed (B) Small brownish needles — $(Me_2S)_2Pt(NO_2)_2$ Formed from $(Me_2S)_2PtSO_4$ and potassium nitrite (B) Formed Small white plates, soluble in chloroform -(Me₂S)₂PtSO₄2aq [91°] Formed from silver sulphate and (Me₂S)₂PtCl₂ Yellowish crystalline mass, v sol water $-(Me_2S)_2PtCrO_4$ reddishbrown pp got by adding K_2CrO_4 to a solution of (Me,S),PtSO. Sl sol water, insol alcohol and chloroform

Methylo-sodide SMe,I Tri methyl-sulphine woulde Formed, even in the cold, by the

union of Me2S with MeI (Cahours, O R 80, 1817, 81, 1163, A Ch [5] 10, 13, A 135, 855, 136, 151) Formed also by heating MeI at 100° with ppd As₂S, or with Na₂S (Klinger, B 15, 881, A 252, 357) and by heating SEt, I with MeOH at 140° (Klinger a Maassen, A 252, 252) Large prisms (from water), v sol hot water, sl sol alcohol, insol ether Its aqueous solution is partially decomposed on evaporating at 100°, forming Me₂S and iodine Moist Ag₂O yields SMe, OH, a strongly alkaline base whence the other salts may be prepared by neutralisation with acids An aqueous solution of SMe, I gives with alcoholic HgCl, app of Me, SIHgI, which forms pale yellow needles, nearly insol water and ether, sol alcohol (Patein, Bl [3] 2, 159) Bromine forms Me, SIBr, which separates from hot alcohol in orange-red crystals [95°] which in alcoholic solution give with platinic chloride a pp of (Me,SCl)₂PtCl₄ (Dobbin a Masson, C J 47, 56) Tri methyl sulphine di bromo-iodide is converted by dry NH, into Me, SIBr, N, H, an amorphous light green mass [75°-80°] Chlorine forms Me, SICl2, which separates from alcohol in yellow crystals [104°], converted by aqueous ammonia into iodide of nitrogen and by gaseous ammonia into Me₃SICl₂2NH₃ an unstable compound which loses ammonia and absorbs water when exposed to air (D a M) The compound (Me,SI),As,I, is formed by heating As,S, with MeI at 100° and crystallises in blue black needles (Klinger a Maassen, A 252, 260) The com pound Me,SISnI, crystallises in yellow needles, sl sol cold water The compound (Me,SI),CdI, formed by heating CdS with MeI at 100°, crys tallises from water or alcohol in white needles, melting at 185° when slowly heated and 195° when quickly heated, and converted by aqueous CdI₂ into Me₃SICdI₂ [168°]

Methylo chloride Me, SCI From the base HCl Deliquescent prisms Gives the salts and HCl Deliquescent prisms (Me,SCl),PtCl, crystallising from hot water in sparingly soluble orange-yellow prisms and Me.SAuCl, crystallising in thick prisms, v e sol water Me₃SCl shaken with an ethereal solution of rodine yields reddish black crystals of Me, SI, Cl, which is probably also formed from Me,SI and ICl (Dobbin a Masson) Me, SCl is converted by ICl into Me,SICl. Dry chlorine forms Me.SCl., a yellow liquid, solidifying on exposure to air Decomposed by water, alcohol, and ether, into

Me,SCl and chlorine

Methylo-bromide Me,SBr Formed from Me,SOH and HBr Also formed from Me,S and MeBr Prisms, v sol water Converted by rodine in ethereal solution into Me,SBrI... With ICl it forms Me SCIBrI as yellow crystals [87°], completely decomposed at 190°

Methylo - sulphydrate Me₃S SH aq From Me₃S OH and H.S (Brown a Blackie, J pr [2] 23, 395)

Methylo sulphide (Me,S).S Tri-methyl sulphine sulphide An aqueous solution of this body may be got by saturating one half of a conc solution of Me₃S OH with H₂S, and adding the other half This solution, if allowed to evaporate in dry air or in coal gas, when it reaches a certain strength forms Me,S, thus $(Me_3S)_2S = 3Me_2S$ (Crum Brown a Blankie, Pr E 9, 563, C N 37, 130) On gently heating a solution of (Me.S).S in a sealed tube, Me.S separates as an upper layer The aqueous solution has the characters of an alkaline sulphide, dissolving sulphur (forming (Me₃S)₂S₃) and Acids decompose it with evolution of

Methylo-throsulphate (Me,S)2S2O3 aq Formed by exposing an aqueous solution of (Me,S),S to atmospheric oxidation Formed also by exposing (Me,S),S, to air Hygroscopic four-sided prisms, sl sol alcohol Decolourises At 135° it is decomposed a solution of iodine into Me2S and Me3S O SO2 SMe, a white crystal line mass [100°] which does not act upon iodine but slowly oxidises to sulphate (Crum Brown a Blaikie, J pr [2] 23, 395) Methylo - sulphite (Me₃S)₂SO₃ xaq

Formed from the hydroxide by saturating one half of its solution with SO2, and adding the other half (Crum Brown a Blankie, Pr E 9, 712) Crystals Gives off water of crystallisation at 140° At 170° it gives off Me₂S, leaving a liquid residue, which solidifies on cooling, and

ns apparently (Me₃S)SO₃Me
Methylo - dithionate $(Me_8S)_2S_2O$ 6aq Formed from Me.S OH and dithionic acid Deli-quescent cubes, insol alcohol Decomposes at 220° into SO₂ and (Me₃S)₂SO₄, and the latter then further decomposes into Me,S and Me,S SO,Me

Methylo - metaphosphate Me_sS PO_s From AgPO, and Me,SI Hygroscopic glassy mass, giving off Me2S on heating

Methylo ferrocyanide

(Me,S),FeCy,9aq From Me,SI and silver ferro-Transparent green plates, which lose their water in a desiccator, and then give off Me₂S at 220°

Methylo-ferricyanide (Me,S), FeCy, 7 aq From I From Me SI and silver ferricyanide (Crum Brown a Blaikie, Pr E 10, 258) Pale orange efflorescent plates

The methylo-chromate and methylo-

-iodate explode at 140°

Methylo-carbonate (Me,S)2CO3 Formed from Me₃SI and Ag₂CO₃, the liquid being evaporated to a syrup and left to crystallise over H₂SO₄ Deliquescent prisms, with strong alkaline reaction At 100° it is split up into CO₂, water, Me,S, and methyl alcohol

Methylo-oxalate (Me₃S), C₂O₄ aq Formed from Ag₂C₂O₄ and Me₃SI Deliquescent crystals Split up at 140° into Me₂S and methyl oxalate Methylo-acetate *Me₃S OAc Formed

from Me, SI and AgOAc (Crum Brown a Blankie, Pr E 10, 53, C N 39, 51) Split up at 100° into Me₂S and MeOAc

Methylo benzoate *Me, SOBz From the nodide and AgOBz Thin plates (from alcohol) Decomposed by heat into Me₂S and MeOBz

Ethylo-rodide SMe, Etl Di methyl-ethylsulphine volide [110°] Formed either from Me₂S and EtI or MeEtS and MeI (Klinger a Maassen, A 248, 212, 252, 246, of Kruger, J pr [2] 14, 193) Hygroscopic crystalline mass, v e sol alcohol, insol ether Yields on distillation Et,SI and Me,SI In altoholic solution it reacts with AgCy at 90°, forming SMe_EtCyAgCy, a deliquescent crystalline body, v sol alcohol, insol ether, and decomposed by heat into AgCy and SMe₂EtCy (Patein, C R 106, 861) Forms the following compounds — (Me₂SEtI)₂CdI₂ [180°], crystallising in small

needles, sl sol water -Me₂SEtICdI₂ [99°], crys tallising from hot cone CdI_Aq in long needles.

-Me₂SEtIHgI₂. [66°] (Patein, Bl [3] 2, 159) Ethylo-chloride Me₂SEtCl The following compounds of this body have been prepared (Klinger a Maassen, A 243, 212) — Me₂SEtCl(HgCl₂)₂ [119°], long needles, insol. hot water—Me₂SEtCl(HgCl₂)₈ [200°], white crystalline powder, slightly soluble in water — (Me₂SEtCl)₂PtCl₄ [c 213°], small orange crystals, sl sol water, insol alcohol and ether — Me_SEtClAuCl, [244°], long yellow needles, m sol hot water

Di methyl disulphide C₂H₈S₂ is Me₂S₂, (117°) (C), (112° at 744 mm) (Pierre, A 80, 128) S G ¹⁸ 1 046 (C) V D 3 30 S V 100 6 (Lossen, A 254, 71) Formed by passing McCl through an alcoholic solution of K2S2, or by distilling $Ca(SO_4Me)_2$ with K_2S_2 (Cahours, A Ch [3] 18, 157, A 61, 92) Liquid, with intolerable odour of onions, v sl sol water, miscible with alcohol and ether Burns with blue flame Chlorine converts it first into crystalline Me₂S₂Cl₂, and finally into a liquid mixture of (CCl₃)₂S and SCl₂ (Riche, A 92, 356) Dilute nitric acid converts it into methyl methane thiosulphonate MeSO₂ SMe

Derivative - v PER - CHLORO - METHYL DI-

SULPHIDE

Di-methyl trisulphide Me₂S₃ (170°) at 760 mm S G $^{\circ}_{0}$ 1 2162, $^{\circ}_{0}$ 1 2059, $^{\circ}_{0}$ 1 199 Formed together with Me₂S₄ and S from methyl mercaptan and S₂Cl₂ (Klason, B 20, 3414) Formed also from MeCl and K₂S₅ (Cahours) Pale yellow liquid, with very disagreeable odour

Derivative -v Hexa bromo di methyl tri-

METHYL SULPHITE C₂H₆SO₃ i e SO(OMe)₂ (121 5°) SG 162 1 0456 VD 3 68 (calc 3 80) Formed by the action of methyl alcohol on S2Cl2 or on SOCl₂ (Carius, A 110, 209, 111, 93) Colourless liquid, with pleasant odour, miscible with alcohol and ether It dissolves slowly in water with evolution of SO₂ and formation of MeOH

METHYL SULPHOCYANIDE C,H,NS 1 e MeSCy (138°) SG 12 1115 (C), \$\frac{1}{2}\$ 1069 (Nasını a Scala, \$G\$ 17, 66) R_a 33 8 S V 781 (Lossen, \$A\$ 254, 73) HFp -31,410 HFv -31,990 (Thomsen, \$Th\$) Obtained by distilling potassium sulphocyanide with calcium methyl sulphate (Cahours, A Ch [8] 18, 261, A 61, 95) Liquid with alliaceous odour, v sl sol water, miscible with alcohol and ether Boiling nitric acid oxidises it to Chlorine acts upon it methane sulphonic acid according to the equation -3MeSCN + 11Cl2 = $\text{Cl}_2\text{Cy}_3 + 2\text{CSCl}_4 + \text{CSCl}_2 + 9\text{HCl}$ (James, J pr [2] 85, 462) Cold aqueous KOH does not attack it, but alcoholic potash forms Me₂S₂, ammonia, KCy, and K₂CO₂ Alcoholic KSH forms KSCy and Me₂S When heated at 180° it partially changes to methyl thiocarbimide

Methyl polysulphocyanide (CH,CNS), (?) [188°] Prepared by heating methyl sulphocyanide to 180° with a trace of HCl (Hofmann, B 13, 1849) Sublimable Colourless crystals Sol acetic acid, insol acids and alkalis By heating with alcoholic NH2 to 150° it gives a well-crystallising base

METHYL-SULPHONAMIDES v. METHYL SULPHAMIDES

DI-METHYL-SULPHONE C2H6SO2 r e Me_2SO_2 . Mol w 94 [109°] (238°) R_{∞} 82 09 in a 246 aqueous solution (Kanonnikoff, J R 15, 451) Formed by oxidising Me₂S with fuming HNO₃ (Saytzeff, A 144, 148) or with aqueous KMnO, (1 30) (Beckmann, J pr [2] 17, 454) Thick needles (from alcohol) Not affected by reducing agents

DI METHYL-SULPHONE DI-CARBOXYLIC ACID O₂S(CH₂ CO₂H)₂ Sulphono di acetic acid [182°] Formed by oxidation of thio di glycollic (sulphido diacetic) acid in alkaline solution with KMnO₄ (Lovén, B 17, 2817) Long trimetric tables V sol water, alcohol, and ether At 200° it splits up into di methyl sulphone and

CO₂ Salts —A"Ba 5aq fine felted sparingly soluble needles —A"Ba aq small prisms

Ethyl ether A"Et, thick oil Amide O₂S(CH₂ CONH₂), glistening plates, v sol hot water, slightly in cold

METHYL-SULPHONIC ACID v METHANE SULPHONIC ACID

METHYL SULPHOXIDE (CH,)2SO nitrate (CH,), SOHNO, is formed by oxidising methyl sulphide with cone HNO, Aq and crys tallises in deliquescent needles, whence BaCO3 sets free the oxide (Saytzeff, A 144, 148) Oil, v sol water Solidines when strongly cooled Beduced by zinc and H2SO, to methyl sulphide Me_2S

METHYL-SULPHURIC ACID v METHYL SULPHATES

METHYL SULPHYDRATE v METHYL MER CAPTAN

METHYL-TARCONIC ACID v NARCOTINE

DI-METHYL TARTARIC ACID C₈H₁₀O₆ 1 e CO,H CMe(OH) CMe(OH) CO H Di oxy di methyl succinic acid Formed, together with lactic acid, by the action of zinc and a little HClAq on pyruvic acid in alcoholic solution Syrup—KHA" small sux sided plates, v sl sol water—K,A" needles, m sol water— BaA" daq prismatic needles, sl sol water — *CaA" crystalline pp, nearly insol water

METHYL-TAURINE vMETHYL AMIDO ETHANE SULPHONIC ACID

METHYL-TAURO CYAMINE v Methyl GUANIDO ETHANE SULPHONIC ACID

METHYL TEREPHTHALIC ACID v Tolu ENE DICARBOXYLIC ACID

Di methyl terephthalic acid v XYLENE DI CARBOXYLIC ACID

METHYL-TELLURIDE v TELLURIUM, OB-GANIC COMPOUNDS

METHYL TETRADECYL KETONE C16H2 O 2 & CH₃ CO C₁₄H₂₉ [43°] (231°) Formed by distilling a mixture of barium pentadecoate and barium acetate (Krafft, B 15, 1707) myristic and acetic acids on oxidation

DI-METHYL THETINE C.H.SO. . .

CH₂ < SMe₂ > O Anhydride of the methylo-

hydroxide of the methyl derivative of thiogly collic acid Obtained by decomposing its hydro bromide with moist Ag.O, or its sulphate with

baryta (Crum Brown a Letts, Tr E 28, 571, B 6, 1384, 7, 695) Crystals (containing aq) Hygroscopic, but gives up the water over H₂SO₄ V sol water, m sol alcohol Neutral in reaction Decomposes when heated into CO2 and (Me_sS)₂CO_s, the methylo-carbonate of di methyl sulphide Yields di methyl sulphone when oxidised by KMnO. The following compounds may be styled its salts —Me₂SBr CH₂ CO₂H. Formed from bromo-acetic acid and Me₂S Large deliquescent rectangular plates (from al cohol) Acid to litmus With lead oxide it forms C4H8SO2PbBr2 Decomposed by heat or by boiling alcohol into SMe₂Br, methyl bromide, and S(CH₂CO₂H)₂ (Letts, Tr E 28,591) Yields and S(CH₂ CO₂H)₂ (Letts, Tr E 28,091) fields methane sulphonic acid on oxidation (Letts, Tr E 28,601)—(C₄H₂SO Br),PtBr₄(?) dark red crystals—Me₂SCl CH₂ CO H Formed from the sulphate and BaCl₂ Deliquescent crystals, v sol water, v sl sol. alcohol—(C₄H₂SO₂)₂HI(?)—Me₂SI₄CH₂CO₂H Formed by leaving discretization of the sulphate and context, with dulta HIAC methyl thetine in contact with dilute HIAq Crystals, insol water, sol alcohol and ether-SO₄(SMe CH CO₂H) Dr methyl thetrne sulphate Formed from Me₂SBr CH₂ CO₂H and silver sulphate Crystalline mass, sol water, v sl sol alcohol Acid to litmus When heated over 140° it fuses and splits up into CO and (Me₃S) SO₄, the methylo sulphate of di methyl sulphide - Me₂S(NO₃) CH₂ CO₂HMe SBr CH. CO, H and AgNO, Colourless crystals with acid reaction. Yields di methyl sul phone when oxidised by conc HNO.

METHYL - THIALDINE C,H,, NS. Obtained on treating crude thio acetic aldehyde with an aqueous solution of methylamine (W Markwald, B 19, 2378) Long needles (from alcohol), insol water, sl sol cold alcohol, v e sol hot alcohol and ether Its solutions possess a feeble alkaline reaction Volatilises in steam with partial decomposition With acids it forms very soluble salts

μ - METHYL - THIAZOLE C.H.NS 16. $_{\rm CH\ CH}^{\rm S\ CMe} \gg$ N (128° cor) Formed by boiling thioacetamide CH3 CS NH2 with chloro acetal (Hantzsch A 250, 270), or with di chloro di ethyl oxide (Hantzsch, B 21, 943) Mobile liquid, miscible with water Its hydrochloride and hydrobromide form hygioscopic needles. With mercuite chloride it forms compounds melting at 112° and 154° B' H. PtCl. [199°] Hexagonal plates or flat needles (from water) -Picrate [146] Yellow needles, sl sol water, v sol alcohol and benzene

(a)-Methyl-thiazole S—CH CMe N (132°) Obtained by distilling oxy methyl thiszole (from chloro acetone and metallic sulphocyanides) with zine dust (Hantzsch a Arapides, B 21, 942), A 249, 24) Formed also by boiling with alcohol the diazo compound derived from amido methyl thiazole (from chloro acetone and thio urea) (Popp, A 250, 277) Colourless liquid, sinking under water, but slowly dissolving, v sol alcohol and ether The hydrochloride is deliquescent. It forms two compounds with HgCl, melting at 119° and 148° The aurochloride melts at 185°, and the picrate at 174° - B'2H2PtCl. [204°] Orange prisms, m sol water, al. sol.

alcohol.

aμ - Di - methyl - thiazole C,H,NS ιε S CMe N (145° cor) S G 15 1 0601 Formed from thioacetamide and chloro - acetone (Hantzsch, B 21, 943, A 250, 265) Colourless liquid, more sol cold than hot water Reduced in alcoholic solution by sodium to ethylamine and propyl mercaptan (Schatzmann, A 261, 1) -B'HLPtCl, [215°] Prisms, m sol water — B'HCl(HgCl₂), 4aq [110°] White needles, v e sol water — B'(HgCl₂), [177°] Sl sol cold water, v e sol dilute HClAq — Picrate [138°] Methylo-rodide B'MeI Pointed crystals, v sol water

S CMe $\beta\mu$ D₁ methyl-thiazole (150° CMe CH N

cor) Formed by condensing thioacetamide with (a)-chloro propionic aldehyde (Hubacher, A 259, 240) Oil, v sl sol water, v sol alcohol and ether Volatile with steam — B'₂H₂PtCl₅ [202°] -Prcrate [167°]

Tri methyl thiazole C.H.NS ve

S - CMe CMe CMe N (167°) $SG \stackrel{16}{=} 1013$ Formed by heating thioacetamide with chloro methyl ethyl ketone at 100° (Poubleff, A 259, 258) Liquid, m sol cold, insol hot, water - *B'HCl [174°] —B'₂H₂PtCl₆ [233°] —Aurochloride [156°] —Picrate [133°] Mercuric double chloride [119°]

References - METHYL - AMIDO METHYL - THI -AZOLE, METHYL - IMIDO - DI - METHYL - THIAZOLE, OXY METHYL THIAZOLE, and TOLYL AMIDO METHYL-THIAZOLE

METHYL-THIAZOLE CARBOXYLIC ACID

C₂H₂NSO₂ ie CO₂H C CH N [145°] Formed by heating the dicarboxylic acid [169°] at 171° (Roubleff, A 259, 271) Small needles or prisms, v sol cold, v e sol hot, water, m sol alcohol, sl sol ether, almost msol benzene

Methyl-thiazole carboxylic acid

CO₂H C CMe N [257°] Formed by sapon fying its ether with alcoholic potash (Wohmann, A 259, 299) Pearly plates (from water) or needles (from alcohol), sl sol ether and hot water, almost insol benzene

Ethyl ether EtA' $[28^{\circ}]$ (233° 1 V) at Obtained from amido methyl thiazole carboxylic ether by diazotisation, conversion into chloro methyl thiazole carboxylic ether [51°] and reduction of this by zinc dust and HOAc Flat prisms, volatile with steam

Methyl-thiazole dicarboxylic acid

S C(CH₃)N [169°] Formed by condensing thioacetamide with chloro oxalacetic ether and saponifying with alcoholic soda (Roubleff, A 259, 268) Long white needles, v sol cold water, sl sol ether and benzene —BaA"2aq needles.—HgA" 3 aq crystalline pp

Di methyl thiazole carboxylic acid

CO.H C CMe N [227°] Formed by saponifying its ether (R) Silky needles or small prisms, sl sol hot water, m sol alcohol and ether May be sublimed Yields on distillation with lime di methyl thiazole — AgA' white needles, sol hot water — HA'HCl plates Ethyl ether EtA' [51°] (242° cor)

Formed from throacetamide and chloro acetoacetic ether (Hantzsch, A 250, 269) Needles (from ether), insol water, v sol alcohol and ether METHYL - THIAZYL - PROPIONIC ETHER S CMe N

Formed by condensing

CH C CHMe CO, Et

bromo methyl-acetoacetic ether with thioacetamide in the cold (Roubleff, A 259, 262) oil When saponified and heated with lime it yields methyl ethyl thiazole

(aa')-METHYL-THIENYL-GLYOXYLIC ACID

 $C_7H_6SO_3$ so $S < C(CO\ CO\ H)\ CH = SO^\circ$ Formed by oxidising (aa') methyl thienyl methyl ketone

with alkaline KMnO₄ (Ruffi, B 20, 1747) —
CaA'₂2aq needles —Ba'A₂½aq needles —AgA'
(αβ) - Methyl - thienyl - glyoxylic acid
SC₄H₂Me COCO₂H [142°] Formed by oxidising (a) methyl (B) thienyl methyl ketone with an aqueous solution of KMnO and KOH (Rufh, B 20, 1748) Needles (from water), subliming even in the cold

Phenyl hydrazide

H₂Me C(N₂HPh) CO₂H [141°] Crystalline Oxim SC₄H₂Me C(NOH) CO₂H [104°] SC₄H₂Me C(N₂HPh) CO₂H $(\alpha\alpha')$ - Di-methyl- (β) - thienyl-glyoxylic acid

s CMe CH CMe C CO CO.H Formed by oxidation of (aa') di methyl (β) thienyl methyl ketone with alkaline KMnO (Rufh) Oil, slowly solidifying Yields leuco thiophene green when heated with dı methyl anılıne and ZnCl, -AgA

METHYL THIENYL KETONE v THIENYL

METHYL KETONE

(a) METHYL-THIENYL METHYL KETONE C.H.SO re Acetomethul-

e S<C(CO CH₃) CH C(CH₃) = CH [25°] (233° cor) Formed by the threnone action of AcCl on (a) methyl thiophene in pie sence of AlCl₃ (Demuth, B 18, 3025, 19, 1859, Ernst, B 19, 3275) Large tables On oxidation with KMnO4 it yields thiophene dicarboxylic acid

Fuming HNO₃ forms a nitro derivative [121°] Oxim C₂H₈S(NOH) [125°] Needles (from

dilute alcohol)

Phenyl hydrazide C, H, S(N, HPh) [128°]

Needles (from alcohol)

(β) - Methyl - thienyl methyl ketone C_4H_2 SMe CO CH₃ (216° cor) Formed from (8) methyl throphene and AcCl in presence of AlCl₃ (Demuth, B 18, 3025)

 $(a\beta')$ - D1-methyl - thienyl methyl ketone $C_{e}H_{10}SO$ re $S < \stackrel{CMe}{CAc} \stackrel{CH}{CMe}$ or $S < \stackrel{CMe}{CH} \stackrel{CAc}{CMe}$ (227°) Formed by the action of AcCl on $(\alpha\beta')$ di methyl thiophene dissolved in ligroin in presence of AlCl₂ (Zelinsky, B 20, 2019) Liquid sence of AlUl₃ (Zemman, — Coloured red by isatin and H,SO, OH S/NOH) [70°] Needles

Oxim C₂H₁₀S(NOH) [70°] Needles Phenyl hydrazide C₂H₁₀S(N₂HPh) [70°] Di-methyl-thienyl methyl ketone

SC₄HMe₂CO CH₂ (224°) SG ¹⁷1091 Formed from the di methyl thiophene of coal tar by treat ment with Accil and AlCi, (Messinger, B 18, 2301) Liquid Gives a red colour with isatin and H₂SO₄ Oxidised by alkaline KMnO₄ to thiophene tricarboxylic acid

[65°] Oxim C_aH₁₀S(NOH) Needles TETRA-METHYL-THIO-ANILINE v Tetra METHYL-DI-AMIDO-DI-PHENYL SULPHIDE

METHYL-THIOCARBAMINE CYAMIDE v. | CARBIMIDO METHYL THIO UREA

METHYL-THIOCARBAMINE-ETHYL-CY-AMIDE v ETHYL CARBIMIDO METHYL THIO UREA. DI-METHYL-THIOCARBAZIC ACID

C₂H₈NS₂ ie NMe₄ NH CS SH [112°] Formed from di methyl-hydrazine and CS, (Renouf, B

13, 2172) Colourless plates

METHYL-THIOCARBIMIDE CH. N CS Mol w 73 [34°] (119°) V D 2 42 (calc 2 53) S G 4 1 069 R_a 35 75 (Nasını a Scala, G 17, HFp = 24,520 HFv = 25,100HC (gas) 392,000 (Thomsen, Th 4, 197) Formed by the action of AgNO₃ or HgCl₂ on the product of the union of CS2 on methylamine (Hofmann, B 1, 172) Formed also by heating pure methyl sulphocyanide for some time at 180°-185° (Hofmann, B 18, 2196) Pungent crystals Reacts with sodium cyanamide and alkyl iodides, form ing methyl-alkyl cyano thio-ureas Thus CN₂HNa and MeI give CH₃NH CS NCy CH₃ [c 195°], while allyl lodded yields the compound NHMe CS NCyC₂H, [78°], propyl lodde forms NHMe CS NCy C₂H, [91°], and benzyl chloride forms NHMe CS NCy CH_Ph [173°] (Hecht, B 23, 1658)

METHYL THIOCARBONATES

Methyl dithiocarbonic acid C2H4S2O re CH,O CS SH Methyl xanthıc acıd Methyl xanthogenic acid Xantho methylic acid potassium salt of this acid is formed by adding CS, to a solution of KOH in methyl alcohol (Dumas a Péligot, A Ch [2] 24, 55, Desains, A Ch [3] 20, 504) It crystallises in silky fibres, S G $^{15.9}$ 1 6878 (Clarke, B 11, 1505) Indine converts it into (CH₃O CS) S₂ With EtI it yields MeO CS SEt (184°) -PbA'2

Methyl dithiocarbonate CH₃O CS SCH₃ (168°) (8), (171°) (C) SG 12 176 (S), 15 1143 (O) Formed from CH₃ CS SK and MeI (Salomon, J pr [2] 8, 117) Formed also together with CO and S by heating the compound (CH₃O CS)₂S₂ (v supra) (Cahours, A Ch [3] 19,

158)

Methyl trithiocarbonate Me, CS, (200°-205°) S G 18 1 159 Formed by distilling a mixture of concentrated solutions of K2CS, and Ca(SO4Me) (Cahours, A Ch [3] 19, 163) Yellow liquid with pungent odour, nearly insol water, miscible with alcohol and ether Combines with bromine forming red crystals of Me₂CS₃Br₂ (Berend, A 128, 333)

METHYL THIO-COUMARILIC ACID

C₈H₄(CH₃)O CO SH

Ethyl ether C₈H₄(CH₃)O CO SEt [92°], glistening yellow needles, v sol ether, sl sol alcohol Formed by heating methyl-coumarilicethyl-ether with $P_2S_\delta^*$ By treatment with alcoholic KOH it is reconverted into methyl coumarilic acid (Hantzsch, B 19, 2400)

METHYL-THIOFORMALDINE C.H.S.N & & (CH₂)₈S₂NMe [65°] (c 185°) Formed from an aqueous solution of formic aldehyde by succes sive addition of H_2S and methylamine (Wohl, B19, 2346) Needles (from ether) with unpleasant smell, insol water, sol acids and alcohol, v sol Volatile with steam On boiling it is converted into a substance melting at 130°-140° -B'HCl [188°] White needles, v sol water Its solution is ppd by AgNO, HgCl, and platinic chloride.

Methylo-rodide [161,-163°]. B'MeI Slender needles, v sol water Gives rise to B'MeCl and (B'MeCl),PtCl

METHYL-THIOHYDANTOIN C.H.N.SO 2.6. NH $C < \frac{S CH_2}{NMe CO} > (?)$ Formed by warming methyl thio ures with chloro-acetic acid and water (Andreasch, M 6, 840) Thick prisms or needles (from water), sol hot water and alcohol Boiling KOHAq yields thioglycollic acid Nitrous acid forms a nitrosamine C4H, (NO)N2SO which is an orange red powder, sol hot water

(a) D1 methyl-thiohydantoin C₂H₂N₂SO 26. NMe C $\stackrel{\rm S~CH_2}{\sim}$ [71°] Formed by heating di methyl thio urea with chloro acetic acid in aqueous solution (Andreasch, M 8, 408) Long colourless prisms, v sol water, alcohol, and ether Smells like nicotine Hot aqueous alkalis convert it into thioglycollic acid Nitrous acid forms an isonitroso compound C, H, N, SO, [220°

(β) Di-methyl-thiohydantoin

NH C < NH CO >[114°] Formed from diargentic thiohydantoin and MeI (Andreasch, M Thin plates, v sol water, sl sol 8. 416) Oxidised by KClO₃ and HCl to urea alcohol and other products

DI-METHYL-THIONINE C14H15NS 26 C₆H₃ -NHMe Obtained by the action of C₆H₃< -NMe

Fe₂Cl₆ upon methyl p phenylene diamine in the presence of HoS and HCl The free base is a crystalline powder, sl sol ether and alcohol, insol water The blue alcoholic solution has a The hydrochloride is strong red fluorescence easily sol water with a blue colour and reddishbrown fluorescence The hydronodide (B'HI) is a dark-blue powder, sol hot water and alcohol, sl sol cold water, dyes silk blue The free base by boiling with water is converted into methylthionoline with evolution of NH_2Me By treating the product with 70 pc H_2SO_4 a second molecule of NH_2Me is split off and thionol

-0H C_6H_3 S is formed (Bernthsen a Goske, C₆H₃∠ B 20,931)

NHMe METHYL-THIONOLINE No .O

Formed by boiling di-methyl thionine with water, methyl-amine being evolved By treatment with 70 pc H2SO, a second molecule of methyl-amine is split off, and there is formed

C,H, -он (Bernthsen a Goske, thionol No C₆H₃

B 20, 932) Di-methyl-thionoline v METHYLENE VIOLET. METHYL-THIOPARABANIC ACID

C4H4N2SO2 te CS NMe CO NH CO Oxalyl methylthio urea [105°] Prepared by passing cyanogen into an alcoholic solution of methyl thio urea and boiling the ppd CSN2H2MeCy2 with conc. HClAq (Andreasch, B 14, 1447, M 2, 277)
Yellow plates, sol water, alcohol, and ether
May be sublimed Converted by warming with
aqueous AgNO, into methyl parabanic acid
Di-methyl-thioparabanic acid C₄H₆N SO, te

OS NMe CO Throcholestrophane Oxalyl-da methyl-thno-urea [113°] Prepared by passing oyanogen into an alcoholic solution of s dimethyl-thno urea and boiling the ppd cyanide with HClAq (Andreasch) Yellow monoclinic tables, sl sol cold water, v e sol alcohol, and ether Split up by boiling alkalis into di methylthio urea and oxalic acid On heating with BaCO, and water it gives di methyl oxamide and CSO Boiling aqueous AgNO, forms cholestrophane

(a) METHYL-THIOPHENE C, H, S v e

SCMe CH Thuotolene (111°) Occurs in CH CH CH Thuotolene (111°) Occurs in coal tar (V Meyer, B 18, 3009) Formed by the action of sodium on a mixture of (a) iodo thio phene and MeBr (V Meyer a Kreis, B 17, 1502, Egli, B 18, 544) Formed also by the action of P₂S₂ on acetyl propionic (levulic) acid (Kues, B 19, 556) Oil Forms a tri bromo-derivative [87°]

(β)-Methyl-thiophene S<CH CMe Thio

tolene Occurs, together with the preceding isomeride, in crude toluene from which it may be separated by shaking with H₂SO₄, and passing steam through the boiling acid diluted with 20 p c water. The mixture of methyl thiophenes so obtained boils at 113 cor and has a S G $\frac{18}{18}$ = 1 0194 (Meyer a Kreis, B 17, 787, Schulze, B 17, 2853) Formed by distilling sodium pyrotartrate with P₂S₈ (Volhard a Erdmann, B 18, 455) Oil Oxidised by alkaline KMnO₄ to (3) thiophenic acid. Gives a tri bromo-derivative [34°], and a bromo di nitro derivative [125°]

Di-methyl-thiophene C₈H₈S Throxene Crude

hi-methyl-thiophene C₆H₅S Theoxene Crude thioxene is obtained in considerable quantity by passing steam through sulphuric acid used in purifying xylene diluted with 20 pc of water and heated to boiling (Schulze, B 17, 2853)

(αβ') - Di - methyl - thiophene S CH CH CH m Theorene (138° cor) S G 2º 9956 V D 4 02 (calc 3 9) Formed by distilling β acetyl-isobutyric acid with P₂S₃ (Zelinsky, B 20, 2018) Gives on oxidation methyl-thiophene carboxylic and thiophene dicarboxylic acids

Di methyl thiophene $SC_1H_2Me_2$ (139° cor) $SG_{\frac{3}{21}}$ 9777 Formed from iodo (β) methylthiophene, MeI and sodium (Demuth, B 19,

1850) Liquid

(aa') - Di - methyl - thiophene S CMe CH
Thioxene (137° cor) S G 14 9755 Occurs in
coal tar Prepared from crude thioxene by con
version into iodo di methyl thiophene and re
ducing this body with zinc dust and alcoholic
NaOH (Messenger, B 18, 565, 1806) Formed
by heating acetonyl acetone (di methyl ethylene
diketone) CH₂ CO CH₂ CO CH₃ (3 pts) with
powdered P₂S₄ (2 pts) for an hour at 140°-150°,
the yield is 50-60 p c of the theoretical (Paal, B
18, 2252) Formed also from (a) iodo (a') methylthiophene by leaving it for some weeks in contact
with sodium and MeI (Ruffi, B 20, 1747)

Colourless mobile liquid of slight odour Dissolves sulphur considerably Gives a red colour with isatin and H₂SO₄, a violet with phenanthraquinone and H₂SO₄, and a reddish-brown with phenyl glyoxylio acid and H₂SO₄ By KMnO₄ it is oxidised to thiotolene carboxylio acid [142°] The di bromo- derivative melts at [47°–50°], and the tri bromo derivative at [144°] It also forms a bromo- derivative [194°], a second di bromo-derivative [46°], a per-bromo- derivative C₆Br₈S [114°], and oily iodo and nitro- derivatives (Messinger) With phenanthraquinone, HOAc, and H₂SO₄ (Laubenheimer's reagent) it gives a reddish-violet colouration

 $(\beta\beta')$ D₁ methyl-thiophene S<CH CMe

(145°) S G $\frac{23}{23}$ 1 0078 Formed by distilling sodium s-di methyl succinate with P S₃(Zelinsky, B 21, 1836) Yellow oil With a trace of isatin in conc H SO₄ it gives an emetald green colour On oxidation it yields an acid crystallising in needles [139°], sl sol cold water

(αβ) - Di - methyl - thiophene S CMe CMe CH CH om Thioxene (137° cor) S G 21 9938 Formed by distilling β acetyl n butylic acid with P S, (Paal a Puschel, B 20, 2559, Grunewald, B 20, 2585) Colourless, strongly refracting oil In the indophenine reaction it gives a bluish violet colour Laubenheimer's reagent yields a reddish violet colour KMnO, oxidises it to methyl thiophene carboxylic acid and thiophene (ββ') di carboxylic acid

Tri-methyl-thiophene C,HieS & 6

SCMe CMe CH (162°) Formed by distilling CH₃ CO CHMe CHMe CO₂H with P₂S₃ (Zelinsky, B 20, 2025)

Tetra-methyl thiophene C₈H₁₀S 2 e

SCMe CMe (184° uncor) SG 21 9442
Formed from tri methyl thiophene by treatment of this substance (12 g) dissolved in petioleum ether with iodine (48 5 g) and HgO (21 g), distilling with steam, and allowing the iodo tri methyl thiophene which comes over to stand with MeI and sodium (Zelinsky, B 21, 1837) Oil Does not give the indophenine reaction References — DI BROMO METHYL THIOPHENE

and Iodo di methyl phiophene METHYL-THIOPHENE CARBOXYLIC ACID

C₈H_eSO₂ i e S CH CCO,H or

SCC(CO₂H) CH Thut olene carboxylic acid [119°] Formed by oxiding the corresponding dimethyl thiophene with alkaline KMnO₄ in the cold (Zelinsky, B 20, 2020) Needles, sl sol cold water, v sol ether May be sublimed—CaA'₂ 2 aq plates—AgA'

(β)-Methyl thiophene (α)-carboxylic acid SCCO-H) CMe c Thiotolenic acid [144°] Obtained by saponifying its ether, which is formed by the action of ClCO-Et and sodium amalgam upon iodo (β) methyl thiophene (Levi, B 19, 656) Formed also by oxidising (β)-methyl thenyl methyl ketone with alkaline KMnO₄ (Demuth, B 19, 680), and by boiling the amide with alcoholic potash Needles (from water), v sol hot water and alcohol Not at-

tacked by KMnO. - CaA', 4aq plates -BaA'2 5aq small plates, sol water —AgA'

Chloride C.H. MeS COCl (219°) Liquid,

smelling like benzoyl chloride

[119°] (Z) Amide C,H2MeS CONH2 Formed by the action of (Lev1) Cl CONH₂ on (B) methyl thiophene in presence of AlCl. (Zelinsky, B 20, 2024, Gattermann, A 244, 58) Needles (from water), v sol water

(a) Methyl thiophene (a')-carboxylic acid SC(CO,H) CH Methyl throphenic acid oo Thiotolenic acid [142°] (P), [137°] (L) Formed by oxidation of thioxene (from acetonylacetone) with alkaline KMnO₄ (Paal, B 18, 2253) Obtained also from its ether, which is produced by heating iodo (a) methyl thiophene with $ClCO_2$ Lt and sodium amalgam (Levi, B 19, 656) White needles Somewhat volatile with Begins to sublime at c 120° in long needles V e sol alcohol, ether, and boiling water, sl sol cold water. Gives no colour reaction with isatin and H,SO, Oxidised by alkaline KMnO, to the corresponding thiophene dicarboxylic acid —CaA'234aq —A Ag× crystalline powder

Methyl-thiophene carboxylic acid

SCH CH (?) [134 5°] Obtained by oxidising (aB) di methyl thiophene with an alkaline 1 pc solution of KMnO (Grunewald, B 20, 2586)

Di-methyl-thiophene carboxylic acid C H.SO, te S

C(CO H) C CH, [172°] Obtained from its amide by hydrolysis (Zelinsky a Gatter [172°] Obtained from mann, A 244, 59) Needles (from dilute alcohol) -AgA'

1mide C,HMe S CONH, [116°] Formed by acting on di methyl thiophene with Cl CONH2 in presence of AlCla Colourless needles (from water)

Tri-methyl-thiophene carboxylic acid C₈H₁₀SO₂ ie S<C(CO,H) C CH₃ C(CH₄) C CH₃ [208°] Ob tained by hydrolysis of its amide (Gattermann a Zelinsky, A 244, 60) Needles (from alcohol) Amide C, Me, S CONH₂ [147°] Formed by the action of ClCONH₂ upon $(\alpha\beta\beta')$ tri methyl thiophene in presence of AlCla Crystallises from water

(β) METHYL-THIOPHENE SULPHONIC $ACID'C_4H_2MeS SO_3H$ Formed by warming (β) methyl thiophene with fuming H2SO4 (Muhlert, B 19, 1620) Syrup, turning red on exposure to air —KA' aq —ZnA', 3 aq —PbA'' (at 110°)

Chloride C, H2MeS SO, Cl Oil

Amide C,H2MeS SO2NH2 [80°] Crystalline nodules (from ether)

METHYL-THIOPHENIC ACID v Methyl

THIOPHINE CARBOXYLIC ACID METHYL THIO-DIPHENYLAMINE

METHYL IMIDO DI PHENYL SULPHIDE

METHYL DITHIOPHOSPHATES

Di-methyl di thio-phosphoric acid C2H,PO.S2 e e Me2HPO2S2 Formed, together with Me2PO2S2, by the action of P.S. (1pt) on methyl alcohol (5 pts) in the cold (Kowalewsky, A 119, 303)
Thick liquid, soluble in water Decomposes Thick liquid, soluble in water Decomposes below 100°—PbA'₂ prisms (from alcohol) Melts below 100°

Vol III

Trı - methyl dithiophosphate Me,PO,S, Formed as above Liquid, v sl sol water METHYL-THIO-PHTHALIMIDINE C.H.NS

 $\bullet \quad C_{\bullet}H_{\bullet} < \stackrel{C(NMe)}{CH_2} > S$ From thiophthalimidine and MeI (Way a Gabriel, B 23, 2483) Is converted by cone HClAq at 190° into thio phthalide, and by oxidation into o di cyano di benzyl di sulphide (C₀H₄Cy CH₂)₂S₂ [124°] — B'HCl —B'₂H₂PtCl₄ —B'C₈H₂(NO₂)₂OH yellow needles

METHYL-THIO-UREA C2HeN2S 2 e

NH₂CS NHMe [118°] Formed from methyl thiocarbimide and NH₁ (Andreasch, M 2, 277) Prisms, v sol water and alcohol, sl sol ether -B'HI large plates, v e sol water and alcohol Melts below 100° Decomposed by Ag₂O into AgI and methyl-cyanamide (Bernthsen a Klinger, B 11, 492)

Di-methyl-thio-urea C, H, N, Sie CS(NHMe) [51 5°] Formed from methyl thiocarbimide and methylamine (Traumann, A 249, 49, Hecht, B 23, 286, cf Andreasch, M 2, 277) Transparent very hygroscopic plates V sol water, alcohol, and acetone, sl sol ether and benzene, v sl sol. light petroleum

METHYL-THYMO-ACRYLIC ACID v Methylderivative of Oxy METHYL PROPYL CINNAMIC ACID DI-METHYL-TOLANE v DI TOLYL ACETYL

DI-METHYL-TOLENYL-AMIDINE

Hydrochloride C₁₀H₁₄N₂HCl 1 e (NHMe C(C₆H₄Me) NMe)HCl [200 [200°] by adding the hydrochloride of p tolenyl imido ether (EtO C(CeH,Me) NH)HCl to an alcohol solution of methylamine (Glock, B 21, 2654) Long silky needles (from water), v sol water and alcohol—B',H,PtCl, 2aq [95°] Dimetric and alcohol -B',H,PtCl, 2aq crystals

u D₁ - methyl - tolenyl - amidine chloride (NMe C(C₈H₁Me) NH)HCl Formed from the hydrochloride of p tolenyl imido ether and dimethylamine (G) Short prisms

METHYL-TOLINDOLE v DI METHYL INDOLE METHYL-TOLISATIN v Di methyl Isatin DI - METHYL - TOLUBUTYLAMINE

METHYL BUTYL PHENYL DI METHYL AMINE METHYL o TOLUIDINE C.H. N ve

[2 1]C₆H₄Me NHMe (207°) S G 15 973 o Tolyl methyl amine Prepared by the action of (207°) tin and HClAq on the nitrosamine which is ob tained from the crude product of the action of methyl alcohol and HCl on o toluidine (Monnet, Reverdin, a Nolting, B 11, 2278) Obtained also by heating o toluidine hydrobromide (or hydroiodide) with 5 pc more than an equivalent quantity of methyl alcohol for 8 hours at 150° , the yield being 46 pc of the theoretical (Reinhardt a Staedel, B 16, 29) It is also produced by distilling o tolyl amido acetic acid (Widman, J pr [2] 38, 303) Colourless oil — B'2H2PtCl6

Acetyl derivative C.H.Me NAcMe

 (251°) (R a S), (c 260°) (M, R, a N) Nutrosamune $C_{\rm c}H_{\rm 4}{\rm Me~N(NO)Me}$ Converted by alcoholic HCl into the isomeric p-nitroso o methyl-toluidine

[5 1 2]NO C_6H_5Me NHMe or $C_6H_5Me < N \longrightarrow O_6$ which crystallises in green plates, [151°], sol. benzene On boiling with dilute aqueous NaOH D D

it is converted into nitroso cresol and methyl-Potassium permanganate oxidises it to nitro methyl-toluidine [134°] Its hydrochloride C₈H₁₆N₂OH₂Cl₂aq crystallises in yellow cubes [110°], v sl sol cone HClAq (Kock, A 243,

Methyl-m-toluidine [3 1]C,H,Me NHMe (207°) Formed by the action of MeI on m toluidine, and purified by means of the acetyl derivative (Nolting, B 11, 2279) Oil— B'2H2PtCla

Acetyl derivative C.H.Me NAcMe [66°] (c 250°) Sol hot water, alcohol, and ether

Methyl -p - toluidine $[4\ 1]C_6H_4MeNHMe$ (208°) Formed by passing McCl into boiling p toluidine The ethereal extract of the crude product is freed from p toluidine by ppn with H₂SO₄, evaporated, and mixed with Ac₂O resulting mixture of di methyl toluidine and acetyl-methyl toluidine may then be fractionally distilled, and the acetyl derivative saponified by HClAq or NaOHAq (Thomsen, B 10, 1582) Oıl.—B'2H2PtCl6

Acetyl derivative C.H., Me NAcMe [83°] (283°) Plates (from ether alcohol), sl sol.

water, v sol alcohol and ether

Propronyl derivative C₁₁H₁₅NO i e C₆H₄Me N(C₃H₅O)Me (266°-269°) from methyl p toluidine and propionic anyhy dride (Norton a Livermore, B 20, 2270) Con verted by dilute nitric acid into tri nitro methyl p toluidine [130°]

Nitrosamine C.H.Me NMe(NO) [54°]

Insol water, v sol alcohol and ether

D1-methyl o toluidine $C_0H_{13}N_4O_6$ i e [2 1] C_6H_4 Me NMe₂ (183°) Formed by distilling its methylo hydroxide (Thomsen, B 10, 1586, Nolting, B 11, 2279) Prepared by heating o toluidine hydrobromide (or hydroiodide) with a little (5 pc) more than two equivalents of methyl alcohol for 8 hours at 150°, the yield being 93 pc of the theoretical (Reinhardt a Staedel, B 16, 29) Oil Converted by HNOs (SG 15) into di nitro o tolyl methyl nitramine (Van Romburgh, R T C 3, 395) — $B'_2H_2PtCl_6$ -B'2H4FeCy6 white needles -B'2H3FeCy6 42aq yellow unstable crystals (Wurster a Roser, B 12, 1826)

Methylo rodide C, H, Me NMe, I Formed from o toluidine and Mel (Thomsen) It is also a product obtained by heating di methyl amiline methylo-iodide at 220°-230° (Hofmann, B 10,

1585) Needles

Di-methyl m toluidine $[3\ 1]C_6H_4Me\ NMe_2$ (208°) (N, RaS), (215°) (Wurster a Riedel, B 12, 1797) Formed from m toluidine and MeI, or by distilling its methylo iodide (Nölting) When dissolved in H₂SO₄, and treated with HNO₄ (S G 15), it yields $\mathring{C}_0H(NO)$ Me NMe NO₂ (Van Romburgh, \mathring{R} T \mathring{C} 3, 413) $-B'H_2PtCl_6$ -B'₂H₄FeCy₆2aq white needles —B'₂H₃FeCy₆1§aq (Wurster a Roser, B 12, 1826)

Methylo rodide B'MeI Yields

(B'MeCl)2PtCl4. yellow cubes

Di-methyl-p-toluidine [4 1]C₆H,Me NMe, (208°) (R a S , H), (210°) (Van Romburgh) S G 938 Formed, together with other products, by heating dimethylaniline methylo-iodide at 220°-230° (Hofmann, B 5, 707) Formed also by heat ing its methylo iodide with water and PbO and distilling the resulting C.H.Me NMe,OH (Hubner,

Tolle, a Athenstäät, A 224, 337, of Thomsen, B 10, 1586) Prepared by heating p toluidine hydrobromide (or hydro iodide) with rather more (5 pc) than two equivalents of methyl alcohol for eight hours at 150°, the yield being 95 p c of the theoretical (Reinhardt a Staedel, B 16, 29) Oil Converted by fuming HNO, and H2SO, into $C_eH(NO_2)_3Me$ NMe NO_2 (Van Romburgh, R T C3, 404) — B₂H₂PtCl₆ — B₂H₄FeCy₅ aq white powder — B₂H₅FeCy₅2jaq yellow crystals (Wurster a Roser, B 12, 1826)

Methylo-rodride C.H.Me NMe. I Formed from p tolundine and MeI Converted by moist Ag.O into C.H.Me NMe.OH Yields

(C₆H₄Me NMe₈Cl)₂PtCl₄

References - Bromo - DI - METHYL - TOLUIDINE and Nitro methyl-toluidine

DI - METHYL - o - TOLUIDINE SULPHONIC ACID C6H3Me(NMe.)SO3H Formed by sul phonating di methyl o toluidine (Michler a Sampaio, B 14, 2167) Large prisms, v sol hot water, insol alcohol — BaA'₂ plates — CaA'₂ small nodules — ZnA₂ soluble soluble needles

METHYL-TOLUQUINOLINE v DI METHY1 QUINOLINE

METHYL - TOLUQUINOXALINE Dı METHYL QUINOXALINE

METHYL-TOLYLENE-DIAMINE v TOLYL ENF MI FHYL DIAMINE

METHYL TOLYL KETONE v Tolyl METHYL KETONE

METHYL-TOLYL NITROSAMINE v Nutros amine of METHYL TOLUIDINE

DI METHYL-TOLYL PHOSPHINE v Tolyl DI METHYL PHOSPHINE

METHYL TRIDECYL KETONE C15H 7O 1 € CH₈ CO C₁₈H₂₇ [39°] (294°) S G (liquid) 39 8182 Formed by distilling a mixture of barium myristate and barium acetate (Krafft, B 12, 1669, 15, 1724) Yields acetic and tridecoic acids on oxidation

DI - METHYL - TRIDECYL - PYRIDINE $C_{20}H_{85}N i e C_5NH_2Me_2(C_{13}H_7)$ (216° at 13 mm) Formed by distilling its dicarboxylic acid with soda lime (Krafft a Mai, B 22, 1758) B'2H2PtCl6 yellow plates

DI METHYL-TRIDECYL-PYRIDINE DI-CARBOXYLIC ACID $C_5NMe(C_{13}H)(CO_2H)_2$ Formed by saponifying its ether with alcoholic potash — H₂A"HCl crystalline powder, v e sol alcohol

(265° at 10 mm) Ethyl ether Et A" Formed from its dihydride by treatment of the alcoholic solution with nitrous acid (Krafft a Mai, B 22, 1758) Yellowish oil —Et₂A"HCl needles

Di methyl-tridecyl pyridine dihydride di carboxylic ether $C_5 \mathrm{NMe}_2(C_{18}H_{27})H_2(\mathrm{CO}_2\mathrm{Et})_{2^2}$ [60°] Formed by heating a mixture of myristic aldehyde, alcoholic NH, and acetoacetic ether (Krafft a Mai, B 22, 1757) Hard crystalline crusts

METHYL-TROPIDINE v TROPIDINE METHYL-TROPINE v TROPINE METHYL-UMBELLIC ACID v Dr-oxy-

PHENYL-CROTONIC ACID

METHYLUMBELLIFERON v Lactone of DI OXY-PHENYL CROTONIC ACID

a8 - Di methyl - umbelliferon C11H10O2 s.e CMe CMe $C_6H_2(OH)$ Lactone of di-oxy-

٠O. -Ċ0 phenyl pentenoic acid [256°] Formed by the action of H.SO, on a mixture of methyl aceto acetic ether and resorcin (Pechmann a Duisberg, B 16, 2127) Colourless needles of high refrac-tive power Its dilute alkaline and H₂SO₄

solutions have a blue fluorescence Isomeride v Lactone of DI OXY TOLYL CRO TONIC ACID

METHYL UNDECYL KETONE v METHYL HENDFCYL KETONF

METHYL URACIL v DI OXY METHYL PYR-

METHYL - URAMIDO - ACETIC ACID v METHYL HYDANTOIC ACID

m - METHYL - URAMIDO BENZOIC ACID C_pH₁₀N₂O₃ v e HMeN CO NH C₆H₄ CO₂H Formed by the action of methylamine upon cyancaib oxamido benzoic acid NC CO NH C_sH₁, CO_.H (Griess, B 18, 2415) White needles, sol alcohol, v sl sol water—A'Ag white plates METHYL URAMINE An old name for

METHYL GUANIDINE

METHYL UREA C.H.N O 2e NH. CO NHMe [102°] Formed from methyl cyanate and ammonia, or by evapolating a mix ture of potassium cyanate and methylamine sulphate (Wurtz, C R 32, 414) It is also a product of the action of HCl and KClOs on caffeine (Fischer, A 215, 257) It may be pre pared by boiling its acetyl derivative with conc HNO, (Hofmann, B 14, 2734)

Properties - Deliquescent prisms, v e sol water and alcohol Its aqueous solution is neutral to litmus, and yields with nitric acid a pp of the ni trate C2H6N OHNO, [128°], which is converted by furning nitric acid into methylamine and ammonium nitrate (Franchimont,

R T C 3, 220)

Nitrosamine NH2 CO N(NO) Me [124°] Formed by adding NaNO, to a solution of methyl unca mitrate containing ice (Von Biuning, B 21, 1810, A 253, 6) Yellow plates or tables (from ether), v sol hot water, alcohol, and ether Decomposed by long boiling with Exhibits Liebermann's reaction On reducing with zinc dust and HOAc it yields methyl - semi - carbazide NH, CO NMe NH, whence, by heating with conc HCiAq for 6 hours

at 100°, methyl hydrazine is got Acetyl derivative NHAc CO NHMe [180°] Formed from methyl urea and Ac.O Formed by the action of boiling dilute NaOH on a mixture of bromo acetamide (CH, CO NHBr) and acetamide This mixture is prepared by adding aqueous (10 pc) NaOH to acetamide (10 pts) mixed with bromine (13 5 pts) until the colour changes from red to yellow (Hofmann, B 14, 2725, 15, 408) In this reaction methyl cyanate is perhaps first formed and then unites with acetamide Monoclinic prisms (Haushofer, J 1882, 365), sol alcohol, ether, and hot water Split up by alkalis into NH₃, CO₂, methylamine, and acetic acid Boiling cone HClAq forms acetic acid and methyl urea

s Di-methyl-urea C₂H₂N₂O 2e CO(NHMe)₂ [102 5°] (269°) Formed by the action of methylamine on methyl cyanate (Wurtz, Rép

chim pure, 1862, 199) According to Wurtz, the same body when prepared by the action of cold water on methyl cyanate melts at 99 5° and boils between 273° and 288° s Di methyl-urea crystallises easily, is v sol water and alcohol, and forms a hygroscopic nitrate C3H8N2OHNO [c 65°] which is decomposed by fuming HNO. forming methylamine (Franchimont, R T C. 3, 222)

Cyano-acetyl derivative C.H.N.O. 1e NHMe CO NMe CO CH, Cy Formed from s dimethyl urea and cyano acetyl chloride (Mulder, B 12, 466) Crystals, not melted below 260° Gives with bromine water the compound CO NMe CO CBr₂ Conc HNO₃ forms, on

warming, two purple-red compounds

u Di methyl ures NMe₂ CO NH₂ [180°]. Formed by evaporating the mixed solutions of potassium cyanate and dimethylamine sulphate (Franchimont, R T C 2, 122, 3, 222) Large hard crystals with sweet taste, sl sol alcohol and ether Boiling Ac₂O forms NMe₂Ao and cyanuric acid Aldehyde in the cold slowly forms CH, CH(NH CO NMe₂)₂ [160°] Chloral forms CCl, CH(OH) NH CO NMe₂ [156°] and C,H₁,Cl,N₂O₃ [74°] (Van der Zande, B T C 8, 222) Nitrate BHNO₃ [101°] Very large crystals Converted by fuming HNO₃ into dimethyl nitramine —Oxalate B'H₂C₂O₄ aq Decomposes at 105° —Picrate B'C₆H₂(NO₂)₃OH Decomposes on fusion (Van der Zande) [130°]

Tri-methyl-urea C₁H₁₀N₂O i e NMe₂ CO NHMe [76°] (232° cor) Formed by mixing ethereal solutions of methyl cyanate and dimethylamine (Franchimont, R T C 3, 226) Crystallises well from ether, v sol water and alcohol, sol benzene Fuming HNO₃ forms di methyl nitro amine (NMe₂ NO₂) and methyl-

Tetra methyl urea C H₁₁N₂O ie CO(NMe₂)₂. (177° i V) S G ¹⁵ 972) Prepared by passing dimethylamine into a solution of di methyl chloro formamide Cl CONMe, (derived from COCl₂ and NMe H) in benzene (Michler a Escherich, B 12, 1162, Franchimont, R T C 3, 228) Oil, v sol alcohol and ether With conc HNO₃ (S G 15) it yields NMe₂ NO₂ and dimethylamine

Reference - CHLORO METHYL UREA

METHYL URETHANE v METHYL CARB-

(a) METHYL-URIC ACID C.H.O. ... CO NMe CO C NH CO or

co < NH CO C NH > COat 100° Formed by heating at 150° acid lead urate with MeI diluted with ether (Hill, B 9, 370, 1090, Am S [3] 12, 428) Thin prisms, sl sol boiling water, insol alcohol and ether Sol conc H.SO, and reppd by water Oxidised by alka hne KMnO, to methyl allantoin C,H,MeN,O, [225°] KClO, and HCl oxidise it to urea and methyle alloxan By heating with HClAq it is split up into glycocoll, methylamine, CO₂, and NH, (Fischer, B 17, 1776)

Salts—K₂A"3aq Ppd by adding alcohol totsanconsciption KHA"ag Na A"3aq

to its aqueous solution — KHA"aq — Na₂A"3aq — NaHA"aq — CaA"3aq — BaA"4aq — BaA"3aaq:

tufts of delicate needles

Methyl uric acid C₅H₂MeN₄O₃ Possibly identical with the preceding Prepared by rusing urea (3 mols) with methyl amido acetic acid (1 mol), extracting the fusion with water, ppg by ammoniacal AgNO₃ and magnesium mixture, digesting the pp with an alkaline sulphide, filtering, acidifying, and evaporating to a small bulk (Horbaczewski, M 6, 359) Formed also by heating methyl hydantom with amyl allo phanate or with buret (Horbaczewski, M 8, 584) Micaceous scales, sol boiling water and alkalis, sl sol cold water, dilute acids, alcohol, and ether Gives the murexide reaction On heating with HClAq at 170° it gives a product (probably methylamine) which gives the carbamine reaction

(β)-Methyl-uric acid C₃H₁MeN₄O₃ ιε
CO<NHCO C NMe>CO
NHE—C NH

Durin S 05 at 100°

Tri oxy methyl

Formation — 1 By heating the di methyl derivative of chloro di oxy methyl purin with HClAq at 130° (Fischer, B 17, 332)—2 By heating di chloro oxy methyl purin with HClAq at 140° (Fischer, B 17, 1777)—3 Occurs in small quantity, together with a much larger quantity of (a)-di methyl uric acid, by heating neutral lead urate with MeI at 100° (F)

Properties—Slender crystals Sol alkalis Reduces ammoniacal AgNO₃ in the cold Gives the murexide reaction On heating with PCl₃ it yields di chloro-oxy methyl purin On oxidation with HNO₃ or with KClO₃ and HCl it gives methyl-urea and alloxan Split up by heating with HClAq into CO₂, methylamine, NH₃, and

glycocoll

(a)-D1-methyl-uric acid C₃H₂Me₂N₄O₃ * e C₂N₂HMeO₂ C₂ N₂HMeCO [above 340°] S 5 at 100°, 06 at 20° Prepared by heating neutral lead urate with MeI in ether for 20 hours at 165° (Mabery a Hill, Am 2, 306, P Am A 15, 256, B 11, 1329, Fischer, B 17, 1779) Slender monoclinic prisms (containing aq), sl sol water, sol cone H₂SO₄ and HClAq, insol alcohol and ether When heated with cone HClAq at 170° it is resolved into CO₂, ammonia, NH₂Me, and glycocoll Nitric acid oxidises it forming methyl alloxan and methyl urea HCl and KClO₃ form methyl urea, methyl alloxan, and a small quantity of a compound C₃H₄N₂O₃ [160°] The ammonium salt is decomposed on bolling its solution with separation of the free acid (difference from (a)-methyl uric acid)

Salts — K₂A"4aq silky needles, v sol water — KHA"1½aq needles, sol water — Na₂A'4½aq needles, sol water — Na₂A'4½aq needles, sol water — BaA"3aq flat prisms, m sol hot water — BaH₂A"₂3aq

(β)-Di-methyl-uric acid

CO NHE CO C NMe CO Tro oxy-methyl-purm Formed by the action of H₂SO₄ at 140° on the diethoxy-compound obtained by treating di-chloro-oxy di methyl purin with alcoholic NaOH. Formed also by heating di chloro oxy-di-methyl purin with fuming HCl at 130° (Fischer, B 17, 337, 1779) Colourless crystal line powder, v sl sol water, alcohol, and ether Melts at a very high temperature

Reactions —On heating with HCl it is split up into salcosine, methylamine, CO₄, and NH₃

PCl₃ converts it back into di chloro oxy-dimethyl purin. By K_2Cr_2O , and H_3SO_4 it is oxidised to cholestrophane. By oxidation with NO_3 or KClO₃ and HCl it chiefly gives a body $C_1H_{10}N_4O_5$, which forms large colourless crystals [174°], v sol water, and decomposed on boiling with baryta water into mesoxalic acid, urea, and probably di methyl urea

C₈H₁₀N₄O₃ Tri - methyl - uric acid MeN-COHN-CO C-NMe OĊ. OĊ. C-NMe CO HN--NMe∕ MeN-[345°] Formed by heating the lead salt of (β) . di methyl uric acid with methyl iodide (Fischer, B 17, 1782) Fine white needles Sublimable Sol hot water, sl sol alcohol and chloroform Dissolves in alkalis Gives the murexide re action strongly Is very unstable towards acids

C₈H₉O₃N₄Ag fine white needles

Tetra - methyl - uric acid C₉H₁ N₄O₃ is e

CO\NMe CO C NMe CO [218°] Formed by
heating the silver salt of tri methyl uric acid
with methyl iodide (Fischer, B 17, 1784)
Distils undecomposed Fine white needles V
sol hot water, less sol cold, all sol ether Has
no acid properties It is readily decomposed
by alkalis, with evolution of methyl amine It
gives the murexide reaction

METHYL - UVIC ACID C₈H₁₀O₃ 16.

CO,H CH CHMe CO or CO₂H CMe CH₂ CO (CMe CH CMe CH) CO or CMe CH₂ CO (CMe CH) CO (CME

Salts $-(C_8H_9O_3)$ Ba 4aq trimetric plates, a bc = 0 9937 1 4 9021 — A Ca 4aq pearly plates, insol alcohol —A'Ag small prisms (from water)

Ethyl ether A'Et (219°) Colourless oil, heavier than water, volatile with steam

METHYL-VALERIC ACID v Hexoic acid METHYL-VALEROLACTONE v Lactone of Oxy hexoic acid

METHYL-VANILLIN v Di methyl derivative of Protocatechuic aldehyde

DI-METHYL-DI-VANILLIN v Tetra methyl derivative of Tetra oxy di phenyl dicarboxylic aldehyde

DI-METHYL-VINYL-AMINE Methylo-hydroxide C₅H₁₈NO ie NMe₄(C₂H₃)OH Neurne Formed by the action of most oxide of silver on di methyl bromo vinyl methylo bromide NMe₄(CH₂ CH₂Br)Br, the product of the union of trimethylamine with ethylene bromide (Hofmann, C R 47,558, Chem Gaz 1858, 434, Baeyer, A 140, 311) It is also a product of the decomposition of protagon by baryta (Liebreich, B 2, 12), and of the putrefaction of flesh (Brieger, B 16, 1190, 1406, 17, 516, 1137) It is extremely soluble in water, and is extracted from the solution by ether with great difficulty (Marino, G 13, 441) Its solution is strongly alkaline, and fumes with HCl. On evaporating

MILK. 405

its solution it decomposes with evolution of NMe₂. Its aqueous solution is poisonous, and antagonistic to atropine as regards the heart and glandular system (Cervello, *Arch Ital Biol* 7, 232)

Methylo chloride *NMe₃(C₁H₃)Cl Very deliquescent needles — (NMe₃(C₂H₃)Cl)₂PtCl₄ yellow crystals, readily changing to neurine platinochloride (NMe₃(C₂H₄OH)Cl)₂PtCl₄ —

NMe₃(C₂H₃)AuCl, yellow needles

METHYL VINYL KETONE CARBOXYLIC ACID CH₃ CO CH CH CO₂H β-Acetyl acrylic acid [125°] Formed by the action of aqueous sodium carbonate on β bromo acetyl propionic acid CH₄ CO CHBr CH₂ CO₂H in the cold (Wolff, B 20, 425) Plates, v sol alcohol and ether, m sol cold water — CaA'₂ nodules, v sol water — ZnA', amorphous —AgA'₂ stellate groups of needles

Phenyl hydrazide
PhNH N CMe CH₂ CH₂ CO₃H [157°] Formed
from the acid and phenyl hydrazine (Decker, B
21, 2937) or by saponifying its ether Lemonyellow needles, m sol hot water, v sol alcohol
and ether

Ethyl ether *EtA' Phenyl hydrazide PhNH N CMe CH CH CO_Et [117°] Formed from bromo acetyl propionic ether and phenyl hydrazine (Bender, B 21, 2493) Yellowspangles, sl sol cold, v sol hot alcohol On reduction with tin and HClAq it yields methyl indyl acetic

Isomeride v Tetric acid

METHYL-VIOLET A violet dye obtained by the oxidation of di methyl aniline. It consists of a mixture of hexa and penta methyltri amido tri phenyl carbinols $(q \ v)$ (Fischer, B 16, 706, 2904)

DI-METHYL-XANTHINE v THEOBROMINE and Theophylline

Tri-methyl-xanthine v CAFFEINE

METHYL-XYLENE v Mesitylene and ψ Cumene

METHYL-XYLIDINE C9H13N 1 e

C_eH₃Me₂NHMe One of the products obtained by heating di methyl aniline hydro iodide at 225° (Hofmann, B 5, 712) Oil

Di methyl-xylidine $C_{10}H_{13}N$ is c $C_5H_5Me_2$ NMe₂ (196°) SG 9293 Obtained by heating methyl xylidine with MeI (Hofmann, B 5, 712) Oil

Di-methyl-xylidine $C_sH_3Me_2NMe$ (203°) Obtained by methylation of crude xylidine (H) —B'MeI

Di methyl-xylidine C₆H₃Me₂NMe [87°] A by product in the preparation of methyl aniline (Sesemann, B 6, 446) Long needles (from ligroin)—B'EtBr

Di-methyl-xylidine [1 3 4] C₆H₃Me₂NMe (204°) Formed by heating xylidine hydrobromide with MeOH (Baur a Staedel, B 16, 32) Oil—B'₂H₂PtCl₆ small yellow crystals

METHÝL XÝLYL KĚTONE v XYLYL METHYL METONE

METHYSTICIN $C_{15}H_{14}O_5$ (P), $C_{16}H_{18}O_5$ (D) [189°] (D), [137°] (P) Extracted by means of alcohol from Kawa root, the root of Piper methysticum (Gobley, J Ph [3] 37, 19, O'Rorke, O R 50, 498, Nölting a Kopp, Montt Scuent [8] 4, 9, 20, Cuzent, An 1,150, Davidoff, J R

19, 522, Pomeranz, M 9, 863, 10, 785) White tasteless prismatic needles, sl sol hot water, ether, and ligroin, v sol hot alcohol, benzene, and chloroform Dissolves in NaOHAq, but on heating the solution methystic acid is formed On fusion with KOH protocatechuic acid is formed Boiling with KOHAq forms piperonal Alkaline KMnO₄ oxidises it to piperonylic acid

Acetyl derivative C₁₆H₁₆Ac₂O₅ [123°] Benzoyl derivative C₁₆H₁₆Bz₂O₅ [148°] Methystic acid C₁₄H₁₂O₅ [180°] When 10°g of methysticin are warmed with 6 pc NaOHAq 5 g of methystic acid are formed. Methystic acid when heated at 180° evolves CO₂, and the product, after cooling, melts at 93° KMnO₄ oxidises methystic acid to piperonal [37°] and piperonylic acid C₅H₅O₅ [227°] Dilute mineral acids convert it into methysticol. Ac₂O has no action

Methysticol C₁₃H₁₂O₃ & e

CH₂C₀>C₆H₃(C₆H O) [1/2] 4 [94°] Formed by warming methysticin or methystic acid with dilute HCiAq or H₂SO₄ (Pomeranz, M 10, 792) Prisms, insol alkalis, v sol alcohol and ether Forms a phenyl hydrazide melting at 143° According to Davidoff methysticin is C₁₆H₁₆O₃ and is decomposed by alcoholic NH₃ into 'methysticin hydrate' C₅H₁₆O₃ and a compound C₅H₁₁NO₂ which crystallises from water in yellow needles The 'methysticin hydrate' is also formed by the action of alcoholic KOH on methysticin It melts at 159°, forms the crystalline salts KC₅H₅O₃ and Ba(C₈H₂O₃)₂, the ether EtC₈H₂O₄ [100°] and the benzoyl derivative C₄H₂Bz₅O₄ [122°]

METINULIN v INULIN

MICROCOSMIC SALT Sodium ammonium-hydrogen phosphate, Na(NH₁)HPO $_4$ 4 $\rm H_2O$, $v_{\rm e}$ Phosphoric acids and phosphatfs

MILK Milk is the secretion of the mammary glands, to the naked eye it appears to be a white fluid, which in thin layers has a bluish tint Its reaction is alkaline in herbivorous animals and in woman, acid in carnivorous animals Its specific gravity varies greatly, averaging between 1 028 and 1 035 On microscopic examination milk is found to be an emulsion, consisting of a clear fluid which has a light straw colour, in which are suspended numerous minute fat globules of varying size, each inclosed in an envelope of casein Numerous particles of casein and nuclein are also seen (Kehrer, Arch Gynaek 2, 1) The clear fluid in which these float contains proteids, lactose, and mineral salts During the first few days after in solution parturition the milk contains a larger proportion of solid constituents, and is found microscopically to contain, besides the ordinary fat globules, a number of the secreting epithelium cells of the mammary gland of which the proto plasm has undergone fatty degeneration, this secretion has received the name colostrum. The name uterine milk is given to the whitish secretion of the uterine glands which is poured out from them during the early months of pregnancy ın certain anımals

The following tables adapted from Charles's Physiological Chemistry, p 383, after Gorup Besanez, Liebermann, Gautier, &c, give quantitative statements of the constituents which occur in the milk of the commoner animals.—

406 MILK

Constituents		man Colo- strum	A.88	Clow	Goat	Sheep	Mare
Water folids Proteids Fats Milk sugar Mineral salts	87-65 12 35 8-07 8 91 5-01 0 17			86 56 13 44 4 08 4 03 4 60 0 73	86 76 13 24 4 23 4 48 8 91 0 62	83 31 16 69 5 73 6 05 3 96 0 68	82 84 17 16 1 64 6 87 } 8 65

The Ash of Milk in 100 parts

(Wildenstein)	(Weber)	(Haidlen)
4 21 81 59 19 06 18 78 0 87 19 00 2 64 0 10	6 38 24 71 14 39 17 31 1 90 29 13 1 15 0 33	$ \begin{array}{c} 8 27 \\ 15 42 \\ 16 96 \\ \\ 56 52 \\ \\ 0 62 \end{array} $
	4 21 31 59 19 06 18 78 0 87 19 00 2 64	4 21 6 88 81 59 24 71 19 06 14 39 18 78 17 31 0 87 1 90 19 00 29 13 2 64 1 15 0 10 0 33

The most abundant salts are thus the phos phates The excess of potassium over sodium salts is the opposite to what obtains in blood plasma and most other fluids of the body (See also Bunge, Dissert Dorpat, 1874, Zeit Physiol Chem 13, 399) The iron in milk appears to be combined with nuclein (Bunge)

Condensed Milk (Cane Sugar added).

1	Water		29 to 24
8	olids		71 to 76
	Casein		16 to 18
Milk su	Milk sugar		8 to 18
\$4	Cane sugar		27 to 29
	Ash		2 to 25
	P_2O_5		02 to 07

Swiss Condensed Milk (benzoic acid added— Fleischmann)

Water		52 31	Mılk sugar	17 43
Fat		1309	Ash	2 78
Proteid		$12 \ 13$	Benzoic acid	1 74

Gases of milk at 0° 41 metre pressure (Pfluger)

Carbonic acid 7 6 in 100 vols of milk Oxygen 0 1 , , , Nitrogen 0 7 , ,

Certain preparations (Koumiss, Kephir) are now made from mare's and cow's milk, in which the alcoholic fermentation is allowed to take place, and which are valuable stimulants in cases of disease, especially of disordered digestion (for references on this subject v Maly's Jahrsber 14, 167)

The proteids of milk — The most abundant is casem. This is coagulated by rennet, and the more soluble precursor in the milk of the curd should be more accurately called casemogen (v Proteins) Albumin (lact-albumin) which is very similar to serum albumin is also present. Other proteids have also been described in milk, but their presence is doubtful, thus peptone is described by Sohmidt Mulhem (Pf. 28, 287), by Dogiel (Zeit Physiol Chem. 9, 591), and by Biel (Maly's Jahrsber. 15, 198), hemi allumose by

J Schmidt (Maly's Jahrsber 14, 175) proteids appear to be primary albumoses formed by the acidification and boiling employed to separate the casein and albumin (Neumeister, Zert Biol 24,271) True peptone is always ab sent (Neumeister, loc cit, Sebelien, Zeit Physiol Chem 13, 135, Halliburton, Journ of Physiol 11, 449) Whey proteid (Hammarsten), the lactoprotein of some observers, is a by product of the action of rennet on caseinogen. Two other proteids, lacto globulin, which is identical with paraglobulin (J Sebelien, Maly's Jahrsber 15, 184), and lacto syntonin, which resembles acid albumin in its properties (J Biel, lc), are also stated to occur in small quantities, but the evi dence that they exist is not conclusive (Halliburton, lc) In koumiss the proteids are stated to consist of albumin, syntonin, and peptone (A Dochmann, Maly's Jahrsber 11, 190) In colos trum casein is absent, or nearly so, being replaced

by globulin (Sebelien)

The fats of milk — When milk stands, some of the fatty globules rise to the surface, and some of these are possibly freed from their proteid casing (Muller), this forms the layer of cream Butter is the name generally given to the fat itself, which is separated from the milk globules by mechanical agitation (churning), a certain amount of casein is, however, generally present in butter, and about one third of the fat of the milk remains in the butter milk The fats piesent are olein, much palmitin, much less stearin, and about two per cent of the total fats consist of the triglycerides of butyric, caproic, and caprylic acids, with traces of myristic and arachidic acids Cow's butter contains about 68 per cent palmi tin and stearin, 30 per cent olein, and 2 per cent the other fats just mentioned Rancidity is due to the development of free fatty acids, acrolein, &c, and, according to Hagemann, of lactic acid from the lactose admixed with fat in the butter

Lactose or milk sugar $(C_{12}H O_{11})$ may be ob tained from milk by evaporation in rhombic crystals containing one molecule of water of crystallisation, which is given off at 140° dissolves in 6 parts of cold and 2 5 parts of boil ing water It is not so sweet as cane sugar, its specific rotation is $(a)_D = 59 3^{\circ}$ Dilute acids and hydrolytic ferments convert lactose into galactose, which is a glucose, and capable of undergoing the alcoholic fermentation, and which yields mucic acid when treated with nitric acid Lactose re duces alkaline solutions of copper salts, and when oxidised yields mucic, saccharic, taitaric, and oxalic acid Lactose does not itself undergo the alcoholic fermentation, but when much yeast is added fermentation occurs after some time, man nite being formed In presence of casein, &c, it undergoes the lactic acid fermentation, and it is the occurrence of this to which the souring of milk is due

Preservation of milk.—Many different antiseptics have been suggested for the preservation of milk, e.g. salicylic acid, ether, benzene, chloroform, borax, boroglyceride, &c. Preservation is, however, usually effected by evaporating the milk to a thick syrup and adding considerable quantities of cane sugar (For recent papers on this subject v A Mayer, Maly's Jahnsber 12, 168; P Biedert, Jacobi, Dietzell, ibid 169,

O Loew, abid 171, Morgen a Fleischmann,

shid 13, 174, A Baginsky, 175)
Alterations in milk — Many drugs taken in medicinal doses appear in the milk, eg salts of arsenic, antimony, lead, mercury (?), zinc, &c , also organic acids and alkaloids In various diseases the proportion of solids to water and of the different solid constituents is altered, thus in osteo malacia the lime salts are increased Blood and pus may occur in milk, a blue colour sometimes observed is due to the growth of a chromogenic bacterium (vibrio), which, however, appears to be different from that which produces the blue colour in pus (J. Reiset, C. R. 96, 682, 745). In tubercular diseases of cattle there is risk of contamination with tubercle bacilli, milk may also act as the carrier of other infections (scarlet fever, typhoid, &c)

Analysis of Milk

Qualitative -The specific gravity, which is increased by the removal of the cream, and re action are ascertained in the usual way, the milk may then be examined microscopically Casein may be precipitated by acetic or hydrochloric acid, by saturation with magnesium sulphate, or by rennet coagulation The precipitate contains also the fat which may be separated from the casein by ether The filtrate contains the sugar, salts, and the other proteids of the milk, which may be identified by their usual The butter is best obtained from milk by adding half its bulk of 10 pc caustic potash solution, and then shaking the mixture rapidly with twice its volume of ether, on evaporating the ethereal extract the fat is left as a residue The milk globules may be separated from the rest of the milk by filtration through porcelain under pressure

Quantitative -Solids To 10 grains of dry sand add 5 cc of milk, and dry at 100° to con stant weight The increase in weight gives the Below 105 pc of solids in 5 cc of milk solids in cow's milk indicates dilution

Butter This may be estimated by weighing the amount of residue from an ethereal extract of milk to which an equal volume of 10 pc caustic potash has been added The normal minimum for fats is about 2.75 pc (Cameron) There are also various optical methods which depend on the degree of opacity of milk, which values directly as the number of globules present, galactoscopes have been invented by Donné and Vogel (On the lacto butyrometer, an instrument for estimating the fat by the ether method, v Tollens a Schmidt, Maly's Jahrsber 8, 140, Kehrer, 151d 11, 179, F Soxhlet, 180, Egger, 181, M Schmöger, 182) Cream This may be roughly estimated by allowing the cream to rise in a narrow graduated vessel, the thickness of the layer being read off at the end of 24 hours Good milk should yield 10 to 15 pc of cream Pfeiffer's method is a good one, the Proteids casein is precipitated by acetic or hydrochloric acid, and freed from fat by ether, after filtering off the casein the albumin is precipitated in the filtrate by boiling, and after that has been removed the albumose is precipitated by tannin It must, however, be remembered, as stated above, that albumose is an artificial product Each of these precipitates is collected, dried, and weighed

(Maly's Jahrsber 13, 170, v also Parr, and 15, 185) J Sebelien (Zert Physiol Chem 13, 135) estimates the proteids by the amount of nitrogen in the precipitates produced by various reagents Lactose The casein, fat, and albumin having been removed, the milk sugar is converted into dextrose by boiling with sulphuric acid, and this is estimated by Fehling's solution or by the polarimetric method

[In addition to the papers already quoted abstracts of the most important of recent papers on milk analysis will be found in Maly's Jahrsbericht as follows J Forster, 11, 177, Giunti, 178; Weiske a Kennepohl, 187, de Leon, 12, 151; Kiaach, 155, Stenberg, 161, Emmerich, 165, Fleischmann a Morgen, 166, Jorgensen, 167, F Hofmann, 177, Liebermann, 13, 168, C H Wolff, 169, Schrodt a Haussen, 14, 180, v also Schmidt Mulheim, Pf 30, 602] Fleischmann, Das Molkerenwesen, and Tatlock, The Produce of the Davry, Glasgow, 1888, should be also consulted

MILK SUGAR v SUGAR

MILLET OIL Appears to contain an acid C₁₈H₂₂O₃ On fusion with potash oil of millet yields acetic and lauric acids On distillation it yields an acid $C_9H_{16}O_2$ or $C_{10}H_{18}O_2$ (216°-220°) Oxidation by KMnO₄ forms an hexoic acid $C_6H_{12}O_2$, and two oxy acids $C_{14}H_{26}(OH)_2O_2$ [60°], and oxy hexoic acid [108°], which yields an acetyl derivative C₀H₁₁(OAc) CO₂H [71°] (Kass ner, Ar Ph [3] 25, 1081)

MILLON'S REAGENT A solution of mercuric nitrate containing nitrous acid, prepared by dissolving mercury (1 pt) in HNO, (1 pt) diluted with water (4; pts) It gives a red coagulum when warmed with albumen (Millon, A 72, 349)

MINERAL ACIDS A term sometimes applied to acids formed of elements other than The term is chiefly applied to the stronger commonly used acids, sulphuric, nitric, and hydrochloric

MINERALOGICAL CHEMISTRY logical chemistry is that part of chemistry which relates to the mineral products of nature, it is also a part of mineralogy, the science which treats, not only of the chemical characters of these products, but also of their physical and geometrical characters, of their modes and places of occurrence, and of their classification

Mineral products, as they are found m nature, frequently retain much the same character over a considerable extent of country and sometimes for a considerable depth, to such a product the term rock is applied, and to each kind of rock is given a special name Mineral products are either simple or mixed When simple they cannot be resolved, by mecha nical or optical means, into matter presenting different characters, simple mineral products are briefly designated as minerals Rocks are almost always mixed products Generally the presence of different substances is obvious to the unaided eye, and the constituents can be readily separated from each other by mechanical means From the rock termed grante, for example, may be got at least three kinds of matter: firstly, a substance yielding rhomboidal fragments when broken (felspar), secondly, a glassy substance yielding only irregular fractures

(quarts); and thirdly, a substance which may readily be split into very thin plates (muca). By no mechanical process can these substances be resolved into others having different characters, hence they are termed minerals, and as they present manifold differences from each other they have received distinctive names. Sometimes the composite nature of a rock is not evident until a slice, made sufficiently thin to be transparent, is examined with a microscope Or, again, a rock, as for example marble, may consist wholly of a single kind of matter

All simple minerals having the same essential characters are said to belong to the same species, those belonging to the same species may likewise have one or more unessential, yet more or less important, characters in common, and are then said to constitute a variety of that species

It is the province of the mineralogist to discover what characters are presented by minerals, to name the characters, to determine their relative importance, to name the species and their varieties, to classify the species, and so on Such a study of minerals must have been in progress since the earliest times. Even before 300 BC the study was so far advanced that minerals were classified as metals (i.e. those having a metallic lustre), stones, and earths, the characters then recognised as pertaining to stones, and used in their discrimination, were succinctly referred to by Theophrastus as follows—

'There are in stones of different kinds many peculiar qualities, of which colour, transparency, brightness, density hardness, and the like are frequent, though other more remarkable properties are not so common But besides these qualities there are others such as their acting upon other bodies, or being subject or not subject to be acted upon by them. Some are fusible, others will never liquefy in the fire some may be calcined, others are incombustible to which it may be added that in the action of fire on them they show also many other differences. Some, as amber have an attractive quality. Others serve for the trail of metals, as the Lydian stone. But the most known and general properties of stones are their several fitnesses for the various kinds of work some of them are proper for engraving on others may be shaped by the turner stools, others may be cut or sawn some also there are which no iron instruments will touch, and others which can with difficulty, or scarcely at all, be cut by them.'

In this way it was possible even for the Ancients, without any knowledge of either crystalline form or chemical composition, to determine more or less satisfactorily the species met with in the mineral kingdom

The definition and classification of species by means of what have been termed 'external characters' (such as crystalline form, cleavage, density, hardness, colour, lustre, &c)-ie characters which can be determined without in volving a total change of the characters of the mmeral-had been found so far satisfactory that the external characters were used both for the definition and classification of the species by the best mineralogists even so lately as the early part of the present century The most important of the external characters is now recognised to be the crystalline form shown in the year 1772 that all the crystalline forms of the same substance, whether the substance is natural or artificial, are so closely related to each other that they are derivable by simple laws from a single form, and it has

since been proved that the whole series of crystalline forms of the same substance can be defined by means of numerical values which ix the shape of one of its forms, hence the limits tion of each species to specimens which can be referred to one fundamental crystalline form became a necessity (v CRYSTALLISATION, vol 11 p 278)

The recognition of chemical elements and chemical compounds, and of the constancy of the proportion of the elements in each com pound, the setting forth of the atomic theory and chemical formulæ, and the development of analytical methods, had great influence on the advance of mineralogy When the specimens belonging to a species which had been defined by means of external characters were subjected to chemical analysis, it was discovered that in many cases there was a large variation in the proportion, and even in the nature, of the con stituent chemical elements For a time it was supposed that, while some substances have a great tendency to crystallise, others are comparatively mert, that, for example, the crystalline form of dolomite (carbonate of calcium and magnesium) is due entirely to the crystallising power of the carbonate of calcium, and that the carbonate of magnesium is either a mere inactive inclusion, or so feeble a crystalliser as to be completely overpowered by the carbonate of calcium The explanation of these variations of chemical composition within species, as defined by means of the external characters, was eventually fur nished by the principle of Isomorphism $(q \ v)$, and it then became possible to define a species by means of a combination of only two characters -chemical composition and crystalline form In other words, it was found that all specimens which can be referred to the same fundamental crystalline form and to the same chemical type have all other essential characters in common, though they may differ in the less important ones, such as colour or transparency example, if the forms of crystals can be referred to the same fundamental figure, the differences of crystalline development are themselves un essential, hence the substances popularly known as dogtooth spar and nailhead spar, which can be crystallographically referred to the same rhombohedron, and chemically are car bonate of calcium, are regarded as varieties of the species calcite, which includes all specimens having these two fundamental characters in common Similarly, colour is another unes sential character the specimens belonging to the species fluor, for instance, show a remark able variation in colour In some cases a variety characterised by a particular colour receives a distinctive name, emerald and aquamarine, for example, are respectively dark green and light bluish green varieties of the species beryl is very seldom, however, that varieties are really worthy of being distinguished by special names, and in almost every species the transition from one variety to another is so gradual that it is often impracticable to decide on the single variety to which a specimen may be satisfactorily referred On the other hand there are specimens which, though chemically carbonate of calcium, can all be referred to a single fundamental crystalline form quite distinct from that of

They are therefore regarded as belonging to a distinct species and are grouped together under the name of aragonite such a separation is a legitimate one is shown by the fact that the two species, as thus defined, differ in other important characters, such as cleavage, hardness, specific gravity, optical constants, &c Hence the chemical compound calcium carbonate is said to be dimorphous, but, as already indicated, the difference between the two kinds of substance is much more than one of form Titanic oxide, again, is met with in nature as three different kinds of substance, each presenting its own set of characters, they are necessarily to be regarded as distinct species, and have received the specific names rutile, anatase, and brookite titanic oxide is said to be tri The variety of chemical composition morphous among specimens regarded as belonging to a single mineral species, and which is explicable on the above mentioned principle of isomorphism, is well illustrated by the results of analyses of specimens of tetrahedrite (or grey copper ore) The crystals of this mineral belong to the cubic system and are homisymmetrically developed, being all closely related in figure to the regular tetrahedron, chemically they can be referred to the general formula 4R'S R" S, where R" includes chiefly Cu, Fe, Zn, Ag, and Hg, and R" includes Sb, As, and Bi The composition shows the following variations copper 15 to 42 pc, iron 1 to 7, zinc 0 to 7, silver 0 to 31, mercury 0 to 17, antimony 12 to 30, aisenic 0 to 20, bismuth 0 to $1\frac{1}{2}$, a few of the varieties, those containing noteworthy proportions of silver or mercury, for instance, have been distinguished by special names The difficulty of deciding whether a mineral product is to be regarded as a distinct species or as a variety of another species presents itself in the case of the specimens to which the name of tennantite has been given, crystallographically they show the same relationship to the regular tetrahedron which characterises the specimens of tetrahedrite, and chemically they are represented by the same general formula $4R' \otimes R'''_2S_3$, they are distinguished, however, by the absence of antimony (and bismuth) as in the chemical composition of the specimens belonging to the above crystallo graphic and chemical type there is thus a sudden transition from 12 pc of antimony (generally accompanied by more or less arsenic) to zero, the specimens of tennantite are generally re garded as entitled to rank as a distinct species Similarly aragonite, witherite, strontianite, and cerussite belong to one chemical type R"CO, and are almost identical in their fundamental crystalline forms, for the several minerals R" is essentially Ca, Ba, Sr, and Pb they are regarded as distinct species because in nature there is found no gradual transition of chemical composition On the other hand, the isomorphous rhombohedral carbonates belonging to the above chemical type R"CO₂, where R" is Ca, Mg, Fe, or Mn, present such a gradual shading into each other, both chemically and physically, that a perfect definition of species is impossible Another instructive illustration of this difficulty is furnished by the group of minerals to which the name garnet has been given The garnets crystallise in the cubic system, and in their forms the do-

decahedron is prominently developed, chemically they are represented by the general formula 3R"O R"'2O, 3SiO2 They have in general very similar physical characters, though they differ considerably both in colour and specific gravity. they have in fact every claim to recognition as a natural family or group But the differences of chemical composition are remarkable R" and R" are essentially, for grossularite, Ca and Al, for pyrope, Mg and Al, for almandite, Fe" and Al, for spessartite, Mn and Al, for andradite, Ca and Fe", for bredbergite, Ca, Mg, and Fe", for uvarovite, Ca and Cr As the above kinds of garnet are connected by various transitions, it may easily be imagined that the garnet group presents great difficulty as regards the definition of its species, and that it is possible to introduce a large number of unnecessary names into the science

There are other natural groups or families, however, as for example, the augite, hornblende, scapolite, felspar, mica, chlorite, and tourmaline groups, in which the representation of the chemical composition of the whole group by a single chemical formula presents great difficulties Indeed, the formula which are employed in mineral chemistry are at present for the most part empirical, constitutional formulæ, such as are employed in organic chemistry, are almost unknown. Much work must be done before we obtain a real insight into the structure of the more complex silicates. For attempts in this direction the student may refer to the following.—

Augites and Hornblendes Tschermak's Mineralogische Mittheilungen, 1871–17, Neues J M 1, 43

Scapolites Sitz W 1883 [1st part] 1142 Felspars ibid 1864 [1st part] 566 Micas ibid 1878 [1st part] 5, Am S [3] 38,384

Clintonites Sitz W 1878 [1st part] 555 Tourmalines P 139, 379, 547

Silicates in general Z K 17, 25
Minerals are of interest to the chemist as
the source of the various chemical elements, the
characters of which, and of their combinations,
it is his province to study A few of these ele
ments are found in the uncombined state, notably carbon, sulphur, arsenic, bismuth, copper,
silver, gold, and platinum Some are present
in large proportion in numerous mineral species,
the latter themselves plentifully dispersed through
the earth's crust, others are found in few mineral
species, and these only in small quantities and
in few localities

It is the province of the mineralogical chemist to determine the chemical composition of each species and variety, and to represent it by means of an empirical or constitutional formula. A considerable number of minerals are pure or nearly pure chemical compounds of simple constitution, and these are specially interesting to the chemist, as they often furnish him with beautifully crystallised specimens of compounds which, as laboratory products, are either amorphous or are obtained as minute crystals only with much expenditure of time and trouble, among such compounds we may especially note the sulphides of lead, zinc, copper, iron, antimony, and arsenie, the various sulpharsenites

and sulphantimonites, the oxides of aluminium, iron, titanium, silicon, and tin, various silicates, molybdate, tungstate, and chromate, of lead, tungstate of calcium, the sulphates and carbonates of calcium, strontium, barium, and lead, various phosphates, arsenates, and vana dates, of copper, lead, and calcium

Time and energy are now rarely expended in the chemical analysis of a substance unless there is something extraordinary in its external characters, and it is by means of these characters that it is possible to describe for future recognition the substance of which an analysis has

been made

Mineralogical chemistry deals, too, with the classification of all the chemical compounds met with in the mineral kingdom, in fact, the arrangement in large groups is now generally based on chemical composition, though the definition of the species is made to rest also on the crystalline form. The system of classification now generally adopted is as follows—

Division I Native elements, metallic and

non metallic

Division II The compounds of metals with elements of the arsenic and sulphur groups, viz arsenides, sulphides, arseno sulphides, sulpho salts, and their analogues

Division III Chlorides, and their ana

logues

Division IV Compounds of oxygen (a) oxides, (b) oxy salts, namely, (1) carbonates, (2) silicates and titanates, (3) molybdates and tungstates, (4) chromates and sulphates, (5) borates, (6) nitrates, and (7) phosphates, arsenates, and vanadates

For details v Groth's Tabellarische Uebersicht der einfachen Mineralien, Braunschweig, 1889

The mineralogical chemist observes the re actions of minerals with various reagents, both in the wet and dry way, and on a large or a microscopic scale, and by a classification of reactions he provides means for the determination of the

species by chemical methods

To the mineralogical chemist is further assigned the most important task of discovering the modes in which the various chemical compounds may be produced artificially, and the investigation of the processes and reactions by which these chemical compounds have been actually produced in nature In this respect pseudomorphs (i e minerals presenting a form characteristic not of their own but of some other substance) are of great value They are always results of chemical change, and are produced in various ways Some are merely due to the investment of a substance afterwards removed from beneath the crust, these have been termed For example, hollow, well defined scalenohedra of limonite (hydrated ferric oxide) are met with, they owe their form to crystals of calcite upon which the limonite has been de posited In other cases the original mineral is altered throughout its mass, and suffers a loss of a chemical constituent, as when galena (sul phide of lead) is found with the form of anglesite (sulphate of lead) Or, again, there has been an addition of a chemical constituent, as when chessylite (a hydrated carbonate of copper) is found with the form of cuprite (oxide of copper) Or, again, there has been an exchange of chemi-

cal constituents, as when galena is found with the form of pyromorphite (phosphate and chlor de of lead), or calcite with the form of gypsum Sometimes there is a complete exchange of material without loss of form, as when copper is found with the form of aragonite Pseudomorphs illustrate the decomposing influences to which many minerals have been subjected, and throw valuable light on the order of succession in which, and the conditions under which, par incular minerals have been formed and deposited and in furnishing sure proofs of conversions which we cannot hope to effect in the laboratory, they afford a knowledge of facts which can be arrived at in no other way

The following works, relative to the artificial production of substances met with as minerals, may be consulted —

Fuchs, Die kunstlich dargestellten Mineralien, Haarlem, 1872

Daubrée, Études synthétiques de géologie ex périmentale, Paris, 1879

Fouqué a Lévy, Synthèse des minéraux et des roches, Paris, 1882

Bourgeois, Reproduction artificielle des Miné

raux, Paris, 1884 L F
MINT The oil of spear mint (Mentha viri
dis) contains C₁₀H₁₄O (225°), S G 952, and a
terpene (Gladstone, J 1863, 548, cf Kane, A
32, 286)

Peppermint v Menthol

MOCHYLIC ALCOHOL $C_{28}H_{16}O$ [234°] Pre sent in bird lime as mochyl palmitate $C_4H_{76}O_4$ (Divers a Kawakita, C J 53, 274) Slender lustrous prisms, insol water, v sl sol petroleum ether, v sol ether, m sol alcohol Dissolves like birdlime in conc H SO₄ with a red colour Heated with palmitic acid in sealed tubes to 160° a substance very similar to bird lime is obtained Yields on distillation a hydro carbon C_6H_4

MOLECULAR CONSTITUTION OF BODIES. THEORIES OF The theory of the molecular constitution of matter now univer sally accepted was held long before any crucial proof was given of its necessity For though such phenomena as the enormous changes in volume which take place when a gas condenses to a liquid point most strongly to some such view, they cannot be held to be conclusive, unless it is considered axiomatic that a perfectly homogeneous structure is incapable of dilatation or contraction The first attempt to give more elaborate reasoning in favour of the molecular theory of the constitution of matter seems to have been made by Cauchy, and was founded upon the dispersion which light experiences when it passes through transparent bodies Since the velocity of light when passing through such bodies depends upon the wave length of the light, and also on the nature of the body, Cauchy argued, that since a velocity is not of the same dimensions as a length, the velocity cannot depend upon the wave length absolutely, but must depend merely upon its ratio to some other length, now the only length available is one derived from the body itself, and since the dispersion does not depend upon the dimensions of the transparent body, this length must be one intrinsic to the body, the body therefore cannot be homogeneous and without structure or there would be no such length available; the body must therefore be coarse grained This reasoning, however, is not quite conclusive, for light of different wave lengths has different times of vibration, and the phenomenon of dis persion might be expected if there were any time connected with the structure of the body which could come into comparison with the time of vibration of the light Dispersion proves that the transparent body is coarse grained, either with respect to space or time, but does not prove that it is necessarily coarse grained with regard to space on a scale comparable with the wave length of light In fact, in the theories which have been put forward to explain dispersion, this phenomenon is made to depend upon the ratio of the time of vibration of light to some time of vibration of the molecules of the system A less ambiguous proof of the molecular structure of gases was given by Osborne Reynolds in his paper 'Some Dimensional Properties of Matter in the Gaseous State' (T 1879) This proof was founded on the phenomenon called the 'thermal effusion' of gases This phenomenon is of the following kind —If we have a vessel divided into two por tions by a porous diaphragm, say of stucco or meerschaum, and the gas on one side of the diaphragm is kept at a different temperature from that on the other side, it is found that, in order to prevent the gas flowing from the cold to the hot side of the diaphragm, the pressure of the gas on the hot side must be greater than that on the cold side, and that the difference of pressure required to prevent the flow obeys different laws according as the gas is dense or rare If the gas is dense, this difference of pressure varies inversely as the density of the gas, while if the gas is raie, the difference of pressure varies directly as the density Reynolds found that the density of the gas at which the law changed from one form to the other depended upon the fineness of the pores of the diaphragm, the finer the pores, the gleater was the density at which the law changed Thus, since the law connecting the difference of pressure with the density depends upon the diameter of the poles of the diaphragm, there must be some length in the gas with which this diameter of the pores can come into comparison, the gas must there fore have structure, and since the density of the gas when the law changes is greater for small pores than for large ones, the structure of the gas must be finer at great densities than at low The investigations of Sir William Thom bon (Popular Lectures and Addresses), Lo schmidt, and others, have gone further than this, and have not merely furnished proofs that matter has structure, but have given limits be low which the coarse grainedness of matter cannot lie These investigations are founded on considerations about surface tension, the difference of potential which occurs when two metals are put in metallic connexion, the amount of polarisation at the surface of an electrode and an electrolyte, the viscosity, the diffusion, and the conductivity for heat, of gases It will be sufficient for us to show how one of these leads to a limit for the dimensions of molecular structure, and we will take the one pepending on the surface tension The surface-

tension of a film of liquid is not likely to alter until the thickness of the film falls below the distance at which one molecule ceases to exert an appreciable influence on another, for it is only the molecules within a film of this thickness which can exert any influence on those at the surface, so that if we can find a limit to the thickness of a film which possesses an unaltered surface tension, we shall have a quantity comparable with the distance up to which one molecule exerts an appreciable effect on another When a film is stretched, work is done on it against surface-tension, and this work is stored up in the film, so that if the surface-tension were the same for an infinitely thin film as for one of finite thickness, an infinite amount of work could be stored up in the film greatest amount of energy which can be stored up in, say, a gram of water must be less than the amount required to separate the molecules to such a distance that they no longer exert any influence on each other, but this is exactly what is done when the water is vaporised, so that the greatest amount of energy which can be stored up in a gram of water is less than the amount required to convert it into steam convert one gram of water at 15° into steam requires the expenditure of $621 \times 42 \times 10^7$ ergs If T be the surface tension of water, and if the gram of water is stretched into a thin film whose thickness is x, the work done in stretch ing it is $\frac{2T}{x}$, but this is not all the energy which

is communicated to the film, for, unless heat is supplied to the film as it stretches, it will cool, the amount of heat which must be supplied to the film, when measured in mechanical units, is about half the work done in stretching the film, so that the total energy communicated to the film is $\frac{3T}{x}$, this must be less than the work required

to vaporise the film, so that $\frac{3T}{x}$ must be less than $536 \times 42 \times 10^7$, or putting T at 15° equal to 74, x cannot be less than 8.5×10^{-3} cm, that is, a thickness of 10^{-8} cm must be comparable with the range of molecular action of the water mole

Quincke (P 137, 402) investigated the range of molecular forces, by finding the thickness of a silver film which when deposited on glass just began to alter the capillary ascent or depression of water in contact with the glass. The results of this, and other investigations with a similar object, are summarised in the following extract from a paper by Rucker (C J Trans 1888 260) —

Table of propertus of thm films and of molecular magnitude

Thickness of film = 118×10^{-7} cm

Superior limit to the radius of molecular action, deduced from Plateau's experiments (Statzque des Lequides, 1873, 1 210) on the pressure of a soap bubble, by using Maxwell's theory that the surface tension first diminishes when the thickness of the film equals the range of molecular action, $96 \times 10^{-7} - 45 \times 10^{-7}$

Between these limits the thickness of a film begins to be unstable, that is, the surface tension begins to diminish Hence the radius of molecular action must be $< 96 \times 10^{-7}$ and $> 22 \times 10^{-7}$ cm

50 × 10⁻⁷ cm

Value of the range of molecular action deduced by Quincke (P 137, 402) from experiments on capillary elevation

 $1\overline{2\times10^{-7}~cm}$

Average thickness of black soap films, measured by two independent methods

As the tension of a black film is equal to that of a thick film, the surface tension, which begins to diminish at 50×10^{-7} cm, must increase again, and reach its original value at 12×10^{-7} This is also about the thickness below which, according to O Wiener (W 31, 629), a thin silver plate will no longer produce the same effect on the phase of reflected light as a thick silver plate would do

$$10.5 \times 10^{-7}$$
 cm

Thickness of the permanent water film observed by Bunsen (W 24, 322) on unwashed glass at a temperature (23° C) at which the vapour pressure of water is small

$$4 \times 10^{-7}$$
 to 3×10^{-7} cm

Average distance from centre to nearest centre of molecules in gases under standard conditions, calculated by Meyer (Die kinetische Theorie der Gase)

$$3 \times 10^{-7}$$
 cm

Thickness of metal films required to polarise platinum completely (Oberbeck, W 31, 331)

$$10^{-7}$$
 to 2×10^{-9} cm

Thickness of electric double layer, according to Oberbeck and Falck (W 21, 157) $2 \times 10^{-8} \text{ cm}$

Smallest thickness of silver which affects the phase of reflected light (Wiener, lc)

$$14 \times 10^{-8}$$
 to 11×10^{-8} cm

Diameter of gaseous hydrogen molecule $7 \times 10^{-9} - 2 \times 10^{-9}$ cm

This is given by combining (1) the specific inductive capacity and coefficient of viscosity, (2) the refractive index and coefficient of diffu sion, (3) the law of expansion and the thermal conductivity

Average distance between centre of molecules supposed arranged uniformly in liquids and solids according to Thomson

$$2 \times 10^{-9}$$
 cm

Inferior limit to the diameter of a gaseous molecule according to Thomson These results may be shortly summed up as follows -

10°° cm	1	
118×1	Superior limit to range of molecular action	Plateau. Maxwell.
96-45	Range of unstable thickness begins.	Remold and Rücker
59	Superior limit to range of molecular action	} Plateau.
50	Magnitude of range of molecular action	Quincke
19	Range of unstable thickness ends.	Reinold and Rücker
18	Action of silver film on phase of reflected light alters,	Wiener
105	Thickness of permanent water film on glass at 23°	Bunsen.
4-3	Mean distance between centres of nearest mole- cules in gases at 760 mm	O Meyer

10 ⁻⁷ cm. 3-1 { 1-0·02 { -2 { 14-11 { 07-02 { -02 {	Thickness of metal films which polarise platinum Thickness of electric double layer Smallest appreciable thick ness of silver film. Diameter of gaseous hydrogen molecule Mean distance between centres of nearest liquid molecules Inferior limit to diameter of gaseous molecule	Coberbeck Lippmann and Oberbeck, Wiener Exner O Meyer Van derWaals, W Thomson. W Thomson
----------------------------------------------------------------------------------	--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------	------------------------------------------------------------------------------------------

Having obtained some idea of the coarseness of the structure of matter, we shall now consider various theories of that structure In order to see what has been explained by these theories, and what remains to be explained, let us enumerate the most important properties of matter in that state of aggregation when the properties are the most simple, ie the state of a so called perfect 'gas

1 The relation between pressure, density, and temperature is expressed by the laws of Boyle and Charles, $p = \kappa \rho \theta$, when p is the pressure, ρ the density, and θ the absolute temperature of the gas, and k is a quantity which remains con stant for the same gas For different gases κ is inversely proportional to their combining weights In all such gases there is the same number of molecules in unit volume, provided the piessure and temperature are the same

2 The gases possess viscosity The coeffi cient of viscosity (unless the density is very greatly reduced) is independent of the density, but depends upon the temperature. The most recent experiments show that the viscosity varies as the two third power of the absolute tempera ture (Barus, Bulletin of the U S Geological Survey, No 54, 1889)

3 The gases conduct heat with a facility de

pending on the temperature

4 They diffuse into each other with a rapidity depending upon the density and the temperature

5 They possess specific heats of various kinds, the ratio of the specific heat under con stant pressure to that under constant volume being 1 4 for most gases

6 They exhibit phenomena of the type of those which occur in the radiometer

7 When they are raised to a high temperature they become luminous, and give out rays of definite periods, the periods being independent of the temperature They absorb light of the

same periods as those they give out when hot 8 They possess very different electrical pro For low differences of potential they insulate almost perfectly, but when the electric intensity is raised sufficiently a spark passes through them, and the electricity is discharged

9 The various gases exhibit very different chemical properties

According to the kinetic theory of gases a gas consists of a great number of small particles called molecules, moving about with great velo city in all directions, but continually either striking against each other, or coming so near together that they exert forces on each other which produce effects somewhat similar to those produced by the collision of two elastic balls. This theory has been shown by Maxwell and Clausius (Maxwell's Theory of Heat, O E Meyer's Die kinetische Theorie der Gase) to be sufficient to explain all those properties of gases included under (1) These properties are independent of the nature of the molecule, and of the exact way in which two molecules act upon each other They could be deduced equally well whether we supposed the molecules to be hard elastic spheres, or systems attracting or repelling each other when they come near to gether, or vortex rings When we consider other properties besides those included in (1), we find the explanation less satisfactory The theory gives an explanation of the viscosity, diffusion, and conduction of heat, but the exact way in which these properties vary with the temperature depends upon the nature of the action between the molecules Two cases have been worked out by Maxwell In the first case the molecules were supposed to be hard perfectly elastic spheres, and which only acted upon other mole cules when in collision with them According to this hypothesis, the coefficient of viscosity would be proportional to the square root of the The other case which absolute temperature has been worked out by Maxwell is that in which the molecules are regarded as systems repelling each other with forces which vary in versely as the fifth power of the distance be tween them According to this hypothesis, the coefficient of viscosity would be proportional to the absolute temperature The experiments of Barus (l c) and others show that the coefficient of viscosity obeys neither of these laws, but varies more quickly with the temperature than the result obtained on the first hypothesis, and more slowly than that obtained on the second Neither of these theories of the action of one molecule on another can be the true one Sutherland $(P\ M\ 24,\,113,\,168),$ by considering the results of Thomson and Joule's experiments on the cool ing of gases passing through a porous plug, arrives at the conclusion that the force between two molecules must be inversely as the fourth power of the distance between them The value of the temperature coefficient of the viscosity on this hypothesis has not, however, been worked

The fact that the ratio of the specific heat at constant pressure to the specific heat at constant volume is the same for the perfect gases with the same number of atoms in the molecule has not been explained by the kinetic theory, and in fact the results we should expect from the kinetic theory are so different from those actually observed that they constitute perhaps the gravest difficulty which the kinetic theory has yet encountered. The results to which the kinetic theory leads are easily found. Let T_m be the total kinetic energy of the molecules in unit mass, β the ratio of this to the energy due to the translatory motion of their centres of gravity, p the pressure, v the volume of unit mass, and θ the absolute temperature. Then $T_m = \frac{3}{6} \beta p v$, so that k the specific heat at con-

stant volume will equal $\frac{3}{2} \frac{\beta p}{\theta} v$. If the preserve we kent constant then an addition to the

sure is kept constant, then, in addition to the energy spent in warming the gas, an amount

of work— $p \times$ (change in volume for one degree)—is done, but when the pressure is constant the volume is proportional to the absolute temperature, so that the change in volume for one degree $= v/\theta$. Thus, if k_p be the specific heat at constant pressure, then

$$k_p = \frac{3 \beta p v}{2 \theta} + \frac{p v}{\theta},$$
 so that
$$\frac{k_p}{k_p} = \frac{3}{2} \beta + 1$$
$$\frac{3}{2} \beta$$

or if the ratio of the specific heats be denoted by γ $\gamma = 1 + \frac{2}{3\beta}, \qquad \beta - 1 = \frac{5 - 3\gamma}{3(\gamma - 1)}$

Now $\beta-1$ is the ratio of the internal energy of the molecules to that due to the motion of translation of their centies of gravity, and we see from the preceding equation that this depends only upon the ratio of the two specific heats, the constancy of this ratio for different gases shows that the proportion which the vibratory energy bears to the energy of transla tion must be the same for all such gases, so that at the same temperature the vibratory energy of all these gases must be the same Now the number of lines visible in the spectrum of the various gases is very different, and we should therefore expect the gases to have very different capacities for vibratory energy The fact that it is not so seems to indicate that the vibratory energy is not due, at any rate at low temperatures, to those quicker modes of vibiation which manifest themselves as light, but must be due to some other modes common to all gases This mode in a diatomic gas may, possibly, be the motion of the atoms relatively to each other, and this view is strengthened by the fact that the latio of the vibratory to the translatory energy increases with the number of atoms in the mole-Thus, if we take Dulong's values of the ratio of the specific heats for hydrogen, carbon dioxide, nitrous oxide, and ethylene, the values of the ratio of the vibratory energy to the energy of translation are respectively 75, 11, 11, and 2, thus, for these gases the ratios are very approxi mately proportional to the number of atoms in the molecule, and the result suggests that the vibiatory energy at these low temperatures is that of the atoms in the molecule relatively to their common centre of gravity, and not of the quicker modes of vibiation corresponding to the luminous rays If experiments on the ratio of the specific heats could be made at temperatures high enough to produce luminosity of the gas, it is possible that the results might be different from those made at lower temperatures, and that they might be found to vary from gas to gas

Theories of the Constitution of the Molecule
The kinetic theory of gases, as developed by
Clausius and Maxwell, dealt chiefly with the behaviour of a large number of molecules, and said
little about the constitution of individual molecules Quite recently, however, Sir W Thomson
(Lectures on Molecular Dynamics and the Wave
Theory of Light) and Lindemann (Ueber Molekularphysik, Physikalisch Gesellschaft, Konigsberg, 39 [1888]) have discussed the properties
of a molecule consisting of a number of spherical

shells, one inside the other, each shell being connected to the one next it by an elastic spring The external spherical shell is supposed to be acted on by the ether, or, what is the same thing, by a periodic force whose period is that of the vibrations which the ether is transmitting We may say in passing that many of the results ob tained do not depend upon this special view of the construction of the molecule, but would be true if we supposed the molecule to be a dynamical system whose configuration could be fixed by n co ordinates, that is, a system possessing n degrees of freedom. The behaviour of such systems when light falls upon them is investigated in the papers above mentioned, and expressions are obtained for the refractive index of a medium consisting of molecules of this kind for light of any period These expressions explain the dispersion of light, and the results deduced from them agree with those found by experiment, they also explain the anomalous dispersion of the rays whose periods nearly co incide with those which are absorbed by the medium-a subject which was investigated experimentally for several substances, especially a solution of fuchsine in alcohol, by Kundt and Christoffel—the periods of vibration of the glowing gas being the periods of vibration of the spherical shells which constitute the molecule The nature of the molecules assumed in this theory imposes a limit to the amount of energy due to the relative motions of the shells, for it is evident that the amplitude of vibration of any shell cannot be greater than the difference be tween its radius and that of a neighbouring shell Thus, on Lindemann's theory, the internal kinetic energy reaches a maximum, and when it has reached this maximum any further exposure to light must lead to an increase in the trans latory energy, and thus to an increase in the temperature of the system made up of such mole cules

Lindemann explains the development of heat which occurs on chemical combination by the transference of the internal kinetic energy into translatory energy, the substances after com bination possessing less internal energy than before, the heat being produced by a loss of kinetic energy, and not, as in the ordinary ex planation, by a loss of the potential energy of separation If this view is correct, however, the internal kinetic energy must in certain gases be enormously greater than the translatory energy, thus, for example, in the combination of hy drogen and oxygen enough heat is produced to raise the temperature of the mixture nearly 20,000° C, and even assuming that after combination there is no internal kinetic energy, the internal kinetic energy before combination must be about 70 times the translatory energy It is very difficult to see how this can be reconciled with the value found by experiment for the ratio of the specific heat at constant pressure to that at constant volume

According to Lindemann, the electric properties of bodies are to be explained by internal kinetic energy due to vibrations which are too quick to be visible, in fact, roughly speaking, electricity is ultra violet light. This view is open to many difficulties, one of which is that it would not lead us to expect the great differ-

ence that exists between the electrical properties of the atom and the molecule A molecule seems to be almost electrically neutral, thus it is impossible to communicate a charge of electricity to the molecules of a gas, though when the molecule is split up into atoms it exhibits most energetic electrical properties Karl Pearson (Proc London Math Soc, 20, 38) has developed a theory in which the molecules are supposed to be made up of spheres vibrating in an uncompressible fluid, he obtains results similar to those of Sir W Thomson and Lindemann In fact, as we said before, many of these results do not depend upon the nature of the molecule, but would be true if we supposed the molecule to be a dynamical system possessing n degrees of freedom

Evidence as to molecular structure af forded by the spectra of bodies -If we con sider the oscillations of a dynamical system possessing n degrees of freedom, we find that there are n periods of vibration given by the roots of a determinantal equation, and that the relation between these roots depends on the nature of the system, a system could be con structed having n periods of any given value If, however, the system possesses an infinite number of degrees of freedom, there will be an infinite number of periods, but the periods will be connected by more or less simple relations Thus, if the vibrating system were like a stretched string, the periods would be propor tional to the natural numbers, while if it were like a bar, the periods would be proportional to the natural numbers for the longitudinal and torsional vibrations, and to the roots of the

equation $\frac{1}{x} \left\{ \frac{1}{\epsilon^x} + \frac{1}{\epsilon^x} \right\} = \pm 2$ for the transver

sal vibrations If the system were a circular membrane, the frequencies would be propor tional to the roots of an equation formed by equating a Bessels function to zero If the system were a uniform elastic sphere, the fre quencies would be the roots of a complicated equation given by Chree in the Transactions of the Cambridge Philosophical Society (14, 316, Other periods which have been worked out are those of circular vortex rings frequencies of the higher vibrations about the circular form are proportional to $\sqrt{n} (n-1)$, where n is a large natural number, and the vibrations about the circular cross section are proportional to the natural numbers (J J Thomson, On the Motion of Vortex Rings, 35, 74) Many investigations have been made with the object of finding whether or not there are simple harmonics—that is, frequencies pro portional to the natural numbers -in the spectra of bodies In the case of the spectrum of hydrogen, Johnstone Stoney finds that the wave lengths 4102 37, 4862 11, 6563 93, which occur in this spectrum, are very accurately in the ratio $\frac{1}{33}$, $\frac{1}{27}$, $\frac{1}{20}$ Schuster, however, in his 'Report on the Genesis of Spectra' (B A Reports, 1882) says

'Other writers, as, for instance, Soret (P. M. 1871 464), have from time to time drawn attention to harmonic ratios in various spectra, and the author of this report has during the last ten years collected a large quantity of material bearing on the question The results have, on

the whole, not been favourable to the theory of harmonic ratios. In any spectrum containing a large number of lines it is clear that, owing to accidental coincidences, we shall always be able to find ratios which agree very closely with the ratios of small integer numbers. It is only by means of a systematic investigation that we can find out whether these coincidences are due to any real cause. We must, by means of the theory of probabilities, calculate the number of the coincidences, which we might expect to find on the supposition that the lines are distributed at random throughout the whole range of the visible spectrum. If on calculating out all fractions which can be formed in a spectrum by any pair of lines the number of ratios agreeing within certain limits with ratios of integer numbers greatly exceeds the most probable number, we should have reason to suppose that the lines are not distributed at random, but that the law suggested by Messrs. Lecoq de Bossbaudran and Stoney is a true one

Lecoq de Boisbaudran and Stoney is a true one
'The results of a long investigation conducted in this
manner tend to show that the number of harmonic ratios
is, if anything, smaller than was to be expected on the

The simple harmonic ratio is not, perhaps,

hypothesis of no connexion

the following table -

a priori the most probable relation between the periods Balmei (W 25, 80) has shown that the wave lengths of a series of hydrogen lines are expressed by the formula $\frac{Cm^2}{m^2-4}$, where m is an integer Hagenbach ($Verhand\ d\ Natur$ forsch Ges zu Basel, 1886) has compared the results of this formula with Coinu's measure ments of the wave lengths of the hydrogen lines, the result of the comparison is given in

 $\lambda = 3615 \ 42 \frac{m^2}{m^2 - 4}$

Line	m	Calculated wave length	Observed wave-length	Difference
Ha	3	6562.8	6563 1	+ 3
$H\beta$	4	48606	4860 7	+ 1
H_{γ}	5	43398	4339 5	- 3
Hδ	6	41011	4101 2	+1
$H\epsilon$	7	3969 5	3969 2	- 3
Hζ	8	3888 4	3888 1	- 3
$H\eta$	9	38348	3834 9	+ 1
$H\theta$	10	3797 3	3797 3	0
$H\iota$	11	37700	3769 9	- 1
$H\kappa$	12	3749 6	3750 2	+ 6
Hλ	13	37338	3734 1	+ 3
$H\mu$	14	3721 4	3721 1	- 3
$\mathbf{H}_{m{ u}}$	15	3711 4	3711 2	- 2
	ĺ	1	}	ł

These results seem to show that the hydrogen molecule is a system possessing an infinite number of degrees of freedom, and not a finite number of rigid particles mutually attracting each other

It is worthy of notice that when m is large the formula previously quoted for the frequency of vibrations of a circular vortex ring becomes Cn^2

 $\lambda = \frac{Cn^2}{n^4 - \frac{1}{2}}$ which is of the same type as Balmer's

A very striking feature in the spectra of some elements is the recurrence in the spectra of certain groups of lines—for example, triplets in the magnesium, doublets in the sodium, spectrum—and the most promising way of finding whether there is anything corresponding to overtones in the spectrum would be the investigation of the relation between the frequencies of the lines in these groups as they recur in the spectrum. It is stated by Schuster that no simple harmonic relations exist between these

groups Deslandres (C R 101, 972) has shown that the periods of the recurring bands in the introgen spectrum are connected by a relation of the form An + B, where n is an integer

The first explanation of the existence of these groups which suggests itself is that corresponding to a triplet we have three, to a doublet two, similar systems near together. Each of these systems, if free from the other's influence, would vibrate with the same period, but when placed so near together that they influence each other, the system of three will have three, and that of two will have two, nearly equal periods

The theory of the oscillation of such systems shows that the gravest mode of the combined system will be lower, and the highest higher, than that of the original system. Thus in a triplet corresponding to each line of the original system, there will be three lines If this view is correct, then any 'element' in whose spectrum doublets or triplets occur is capable of being split up into simpler systems, and the lines of the substance into which it is split up will be intermediate between those of the doublets or Thus, we should expect to find a triplets tendency for these doublets to disappear as the Though there does not temperature is raised seem much evidence to show that this tendency is widespread, it does appear to exist in the case of calcium, for in the drawing of the spectrum of this element given in Lockyer's Studies in Spec trum Analysis (191) there is in the violet end of the spectrum a doublet where the spark is taken without a jar in the circuit, but when a large jar is placed in the circuit the doublet is replaced by a single line intermediate to those of the doublet

The widening of the lines of the spectrum of a gas when the pressure is increased might be explained on similar principles A molecule when free from the influence of other mole cules vibrates in certain definite periods, and shows sharp bright lines in its spectrum, when, however, it gets under the influence of another similar molecule its periods are slightly altered, and for each of the original periods we have two periods, the one graver and the other higher than the original period, the departure from the original period depending on the distance between the molecules Thus, in the case of a gas so dense that the molecules influence each other, the molecules, instead of emitting light of a definite period, would emit light of different periods, some higher and some lower than the undisturbed one, thus, instead of a bright line in the spectrum, we should have a luminous band stretching across the original bright line

Connexion between spectra of elements and those of their compounds—One of the most in teresting subjects in connexion with molecular theories, and one from which we may hope to gain great insight into molecular structure, is the connexion between the spectrum of a compound and the spectra of its constituents Mitscherlich showed that compounds have emission spectra of their own. A considerable amount of work bearing on the subject has been done by Glad stone and Dale, Abney and Festing, Kundt, and others, who have investigated the absorption spectra of compounds. But, however important these researches are from other points of view,

they cannot be said to have as yet thrown much light on the structure of matter

A relation between the lines in the spectrum of a compound and the lines in the spectra of its elements, based on a mathematical theory, which, however, does not seem yet to have been published, has been enunciated by Grunwald, who states (P M (6) 34, 354) —

'Let a be a primary chemical element, which is chemically combined with other elements in a gaseous substance A, and occupies the volume [a] in the unit volume of A Let the substance A combine chemically with another gaseous substance B, to form a third C in this combination let the element a pass into a different chemical condition a', giving up (or in exceptional circumstances taking up) a certain quantity of heat in order to permit the new compound to form, and in consequence chemically contracting (or exceptionally expanding). Let the volume which it occupies in the body C, after the new condition of chemical equilibrium has been established, be [a'], then the quotient [a] [a'] is generally a very sumple rational member in accordance with a known fundamental law of chemistry. If this is the case the wave-lengths \(\text{d} \) of the corresponding rays which belong to the element a in the line-spectrum of the free substance A, and are therefore radiated by it are related to the wave-lengths \(\text{d} \) of the corresponding rays which the same element emits in the new chemical condition \(a', in which it exists in the more complex substance \(A \) within the newly formed compound C, as the corresponding rolumes [a] and [a'] and

This relation has been tested in the case of water vapour, as however both this substance and hydrogen have a good many lines in their spectra, it is not surprising that coincidences occur between the observed and calculated values of the wave lengths of the lines in the water vapour spectrum. We must, therefore, suspend our opinion as to the value of the relation given by Grinwald until the theoretical grounds on which it is based have been published. See also Ames (N. 40, 19)

In a binary compound, AB, we may suppose that the atoms A and B are dynamical systems, which in the molecule of the compound are near together, and that the proximity of A causes the periods when B is vibrating by the influence of other systems, and vice versa. Then the theory of the vibrations of such a system shows that if $p_1 - p_2 - p_n$ are the frequencies of A when free, $q_1 - q_n$ those of B, δp_1 , δp_n , δq_1 , δq_n , the increase in the frequencies $p_1 - p_n$, respectively, due to the proximity of the two systems, then

$$p_1\delta p_1 = \frac{f_{11}^2}{p_1^2 - q_1^2} + \frac{f_{12}^2}{p_1^2 - q_2^2} + \dots$$

With similar expression for δq_1 &c The quantities f_{11} are quantities depending on the proximity of the systems

From this relation we see that the effect on the period, say p_1 , of the first system of the existence of a period, say q_2 , in the second, is to quicken the period of the first, if the first is quicker than the second. If we observe the spectra, this result could be expressed by saying that the effect of the annexation was to make the line of B repel the lines of A. Thus on this theory the spectrum of the compound may be got by superposing the spectra of its constituents, A and B, and then supposing the lines of A to repel those of B, and the lines of B to repel those of A, the repulsion increasing with the proximity of the lines. Thus if we take two elements A and B, such that A and B have two lines nearly coinci-

dent, then in the compound A B these lines will be considerably displaced and the distance between them increased

Arrangement of the atoms in the molecule on the supposition that the atoms are vortex rings There is one theory of the structure of the molecule which is worth mentioning, as it affords a possibility of the explanation of that remarkable alternation of properties with atomic weight which is expressed by the periodic law If we assume that a molecule is built up of a number of vortex rings placed close together, then a section of the molecule, by a plane through the centre at right angles to the planes of the ring, will consist of two groups, each consisting of a number of small circles The arrangement of the circles in either group will be very much the same as the arrangement, when in steady mo tion, of the cross sections of the same number of uniform straight parallel voitex columns with circular sections These, when in steady motion, arrange themselves in a definite way, which may easily be discovered without calculation, as the arrangement is very nearly the same as that of the same number of equal uniform parallel mag nets under the attraction of a magnetic pole, some distance away from the nearer poles of the parallel magnets, and of opposite sign to these poles These magnets will take up definite posi tions of equilibrium, under the action of their mutual repulsion and the external attraction The figures of equilibrium of the magnet are given by Mayer (N 18, 259) and Monckman (Proc Camb Phil Soc 6, 169) If we examine these figures, we see that as the number of magnets increase there is a tendency for certain peculiarities to recur, as, for example, the num ber of planes of symmetry, and the nature of the simpler groups of which we may imagine the more complex ones to be made up Thus, if we imagine the molecules of all elements to be made up of the same primordial atom, and in terpret increasing atomic weight to indicate an increase in the number of such atoms, then, on this view, as the number of atoms is continually increased, certain peculiarities in the structure will recur, which in all likelihood would be ac companied by a recurrence of some of the pro perties of the elements

Electrical theory of molecular structure -There is another view of molecular structure which is almost forced upon us by the laws of electrolysis, this is, that the forces between the atoms in the molecule are electrical in their ori On this theory, the atoms in the molecule of a compound are supposed to be charged with definite quantities of electricity, the quantity of electricity on the atom being the same for all elements of the same valency, and being posi tive or negative, according as the element is electro positive or electro negative The charge on an atom of a divalent element is assumed to be twice, and that on an atom of a trivalent ele ment three times, the charge on the atom of a monovalent element (v Von Helmholtz [Fara day Lecture], C J 39, 277) This view of the structure of the molecule at once explains Fara day's law of electro chemical decomposition It also explains the difference which exists between the electrical properties of the molecule and the atom, for in the molecule the positive and ne

gative charges neutralise each other's effect at | points outside the molecule, the free atom is, however, essentially charged and therefore capable of producing electrical effects When we dissociate a gas into atoms, the dissociated gas, on this theory, consists of an equal number of electrically charged particles, some being charged with positive electricity, and an equal number (if the constituents of the molecule are of the same valency) charged with negative electricity. This collection of electrified particles would behave like a conductor of electricity, so that, if this theory of the structure of the molecule is correct, a gas whose molecules are dissociated by heat into atoms ought to be a conductor of elec-J J Thomson (P M [6] 29, 358, 441) has recently made a series of experiments on the conduction of electricity through very hot gases, and has found that while some of these hot gases (hydriodic acid gas, for example) allow electricity to pass through them with ease, others (such as nitrogen) only allow it to do so with great difficulty, and it was found that whenever the electricity passed with ease through a hot gas, the dissociation of the gas could be detected by chemical means. These experiments are, therefore, in accordance with the result of this theory of molecular structure On this view of molecular structure the 'bonds of affinity' of chemists have a distinct physical meaning, as they are the tubes of electrostatic force connecting the atoms

A difficulty which arises on this theory, and one that seems to show that it requires modification, is the existence at low temperatures of what are called by chemists unsaturated compounds For, according to this view of the structure of matter, an unsaturated compound is one in which there are not equal and opposite quantities of electricity in each molecule, so that the molecules of an unsaturated gas, being electrically equivalent to a number of positively and negatively charged particles, ought to be have like a conductor But gases which are unsaturated at low temperatures, such as NO, behave at these temperatures with respect to electricity like saturated gases, they transmit electric induction For example, a gold leaf electroscope will work perfectly well inside a glass vessel containing NO, and its leaves will be attracted by an electrified body outside the electroscope, and a current of electricity cannot be driven through a tube containing such gases by a battery containing only a small number of We must therefore conclude that electricells cally such gases are saturated

Maxwell, in the article on the 'Constitution of Bodies,' Encyclopædia Britannica, introduced the idea that in solids the molecules might arrange themselves in groups, some of which under the action of stresses might split up and form other stable groups in which the molecules are differently arranged, these new groups returning only slowly to their original configuration after the stresses are removed. This behaviour of the molecular groups shows itself in the 'elastic after effect' produced by torsion in metal wires and glass fibres. Ewing (P. M. [6] 30, 205) has lately applied the same idea to explain the behaviour of iron when magnetised, and has devised a model which illustrates very clearly

VOL III.

the breaking up of the old groups and the formation of new ones ${f J} {f J} {f T}$

MOLECULAR WEIGHTS \mathbf{T} he article ATOMIC AND MOLECULAR WEIGHTS, in vol 1, de scribes the limits within which the term molecu lar weight may be applied with safety to solid and liquid bodies (v especially pp 347-350) Since that article was printed, an advance has been made in the methods by which the molecu lar weights of bodies which cannot be gasified without decomposition may be determined. This advance is based, for the most part, on the researches of Raoult As the result of a long series of investigations into the lowering of the freezing point of water and various other sol vents, produced by dissolving therein quantities of various compounds proportional to the formula-weights, or reacting weights, of these compounds, Raoult finds that such quantities of chemically similar compounds generally pro duce equal lowerings of the freezing points of water and some other solvents (Raoult's Memoirs will be found in A Ch , v especially [6] 8,

Let P grams of a compound be dissolved in 100 g of water or other solvent, and let the observed lowering of freezing point of the solvent be C, then $\frac{C}{P}$ is called by Raoult the coefficient of lowering of freezing point for the compound in question. Putting M as the reacting-weight, or formula weight, of the compound, then $\frac{C}{P}M$ is called the molecular lowering of freezing point for this compound

Raoult finds that $\stackrel{C}{P}M$ is generally constant for all the members of a series of chemically similar compounds. Thus, Raoult gives the following values for $\stackrel{C}{P}M$, water being the solution.

19, for many organic compounds,

35, for salts of monovalent metals with monobasic acids,

40, for normal salts of monovalent metals with dibasic acids

Raoult also gives the following values for ${C \over P}M$, benzene being the solvent —

49, for many organic compounds,

25, for the lower members of homologous series of alcohols

Other values for $\frac{C}{P}M$ were found when other solvents, eg acetic acid, were used

Another form in which Raoult's results may be put is the following $-\frac{P}{C}$ = grams of dissolved body, in 100 g solvent, that lower freezing point of solvent 1° Now $\frac{P}{C} \times c = M$, where c = constant determined experimentally for each series of chemically similar compounds, and for each solvent

If the value of $\frac{C}{P}M$ is known for a group of compounds, or if the value of c is known in the

expression $\frac{P}{C} \times c = M$, it is possible to find the formula-weight of a member of this group Thus, in the case of ether, the following data were obtained —

(i) 4 47 g ether were dissolved in 100 g water, the freezing point of the water was lowered by 105°, hence $\frac{C}{P} = \frac{105}{447} = 23^{\circ}$ But the value of $\frac{C}{P}M$ for organic compounds generally dissolved in water is 19, hence, for ether, $M = \frac{19}{23} = 82$

(11) 2 721 g ether were dissolved in 100 g benzene, the freezing point of the benzene was lowered by 1826°, hence $\frac{P}{C}$ =149, ie 149 g ether in 100 g benzene lower the freezing point by 1° But the constant for such organic compounds as the ethers dissolved in benzene is 49, hence, for ether, $M=149\times49=73$

(iii) The value found for $\frac{C}{P}$ when ether was dissolved in acetic acid was 529° But the value of $\frac{C}{P}M$ for organic compounds generally dissolved in acetic acid is 39, hence, for ether, $M = \frac{39}{529} = 74$

The mean of these three results gives 76 6 for the formula weight of ether, the molecular weight of ether gas, determined by applying Avogadro's law, is 74

The empirical law of Raoult-quantities of chemically similar compounds proportional to the reacting weights, or formula weights, of these compounds produce equal lowerings of the freezing points of water and some other solvents-has been developed by van't Hoff, Arrhenius, and others (v especially Z P C 1, 481 [translation in P M, August 1888], and Z P C 1, 631, 2, 284, 491) If an aqueous solution of a substance is contained in a vessel the walls of which are permeable by water molecules but not by the molecules of the dis solved substance, and the vessel is immersed in water, water will enter the vessel, and the pressure on the walls will increase until equili brium results, after which no more water will enter The pressure on the walls of the vessel is called osmotic pressure. If the vessel were furnished with a movable piston, the same condition of equilibrium might be attained, without the entry of water into the vessel, by compressing the solution with a pressure equal to the osmotic pressure With such an arrangement the concentration of the liquid could be altered by increasing or decreasing pressure by means of the piston, as the process is reversible, the second

law of thermodynamics may be applied

The experiments of de Vries (Z P C 2, 415, 8, 103), Pfeffer (Osmotische Untersuchungen
[Leipzig, 1887]), and others, show that the osmotic pressures of dlute aqueous solutions are proportional to the concentrations of these solutions Now, to say that change of concentration of dlute solutions is proportional to the pressure exerted by the solutions, is equivalent

to saying that Boyle's law holds good for dilute solutions Moreover, the proportionality of con centration to osmotic pressure may be deduced theoretically If we assume, as seems justifiable, that osmotic pressure is due to the impact of the molecules of the dissolved substance, then the number of impacts in unit time must be proportional to the number of molecules in unit volume (on this point v L Meyer, Z P C 5, 23, and van't Hoff's reply, Z P C 5, 174, cf Bredig, Z P C 4, 444) But this is the molecu lar conception of gaseous pressure Hence, as in gases volume is inversely as piessure, the same proportionality should hold good in dilute aqueous solutions, in other words, Boyle's law should apply to these solutions Van't Hoff then proceeds to deduce, by thermodynamical reasoning, that osmotic pressure is proportional to absolute temperature, concentration being constant This conclusion is equivalent to saying that the law of Charles holds good for dilute aqueous solutions, masmuch as concen tration of solution corresponds with gaseous volume

The experimental results of Pfeffer and of Soret (A Ch [5] 22, 293) are in keeping, on the whole, with the statement that the laws of Boyle and Charles hold good in dilute aqueous solutions

Solutions which exert equal osmotic pres sures are called sotonic solutions Thermo dynamical reasoning applied to these solutions leads to the conclusion that the osmotic pres sure of a specified mass of a gasifiable substance in dilute solution is the same as the pressure exerted by the same mass of the same substance existing as a gas at the same temperature If, then, osmotic pressure may be substituted for gaseous pressure, Avogadro's law may be ex tended to substances in dilute solution extension of the law of Avogadro is thus stated by van't Hoff 'Equal volumes of different solutions, at the same temperature and osmotic pressure, contain equal numbers of molicules, which numbers are the same as would be con tained in equal volumes of gases at the same temperature and pressure 'This is van't Hoff's law of osmotic pressure Various proofs of the accuracy of this law have been given

To apply this law, it is necessary to find the mass of a substance present in a solution which is isotonic with another solution containing a known mass of a body of known molecular weight The two solutions then contain equal numbers of molecules of the dissolved sub stances, and as the molecular weight of one substance is known, the molecular weight of the other can be found There are many practical difficulties in determining whether or not two solutions are isotonic. Now van't Hoff has shown by thermodynamical reasoning (Z P C 1, 496) that solutions of different bodies in the same solvent, having equal freezing points, are isotonic at their freezing points Put into other words, this conclusion asserts that solutions which have equal freezing points contain equal numbers of molecules in equal volumes, or, that solutions which contain equal numbers of molecules in equal volumes, and are therefore isotonic, have equal freezing points. But this is the law of lowering of freezing points empirically established by Raoult In place of the somewhat vague term reacting weight, or formula weight, used in stating the law (v supra), we are now justified in employing the more definite term molecular weight. This law, as developed by van't Hoff, asserts that the product of the lowering of the freezing point of a 1 pc solution into the molecular weight of the dissolved body is a constant for different bodies dissolved in the same solvent. For solutions of most organic compounds in water, the constant is about 18 9

Van't Hoff then proceeds to show that the molecular lowering of freezing point of a dilute solution bears a simple relation to the latent heat of fusion of the solvent (for proof $v \ Z \ P \ C \ 1,496-7)$ This relation is expressed, for very dilute solutions, by the equation

 $t = 01976 \frac{T^2}{W},$

where t = molecular lowering of freezing point, already expressed as $\frac{C}{P}M$ (p 417), T = freezing

point of solvent stated in absolute measure, and W= latent heat of fusion of solvent in gramunits (cf. Eykman, Z P C 3, 203, and especially ib Z P C 4, 512). If this conclusion is granted, it follows that equal numbers of molecules of all bodies dissolved in the same solvent must lower the freezing point to the same extent, provided the solutions are very dilute

Let us take a case to exhibit the application of the law of molecular lowering of freezing point in the form given to it by van't Hoff Thymol is dissolved in phenol, and the lowering of the freezing point of the phenol is observed. The constant for molecular lowering of freezing point of phenol is flist calculated by van't Hoff's formula the freezing point of the phenol used was 38°, in absolute measure this is 273° + 38° = 311°, the latent heat of fusion of the phenol was found to be 25°, hence

 $t=0197 \frac{311^2}{625}=76$ The solution of thymol used contained 401 g thymol in 7559 g phenol, the freezing point was lowered by 249°, stating these results in parts of thymol per 100 of phenol, we find that 53 g thymol dissolved in

100 g phenol lowered the freezing point through 2 49° Then $\frac{53}{249} = 212$, ic 212 g thymol in

100 g phenol lowered the freezing point through 1° But this quantity, 2 12, is $\frac{1}{76}$ th of the mole cular weight of thymol, therefore molecular weight of thymol = $212 \times 76 = 161$ The mole cular weight calculated from the formula $C_{14}H_{10}O$ is 150

In applying the law of molecular lowering of freezing point it is necessary to work with dilute solutions. The freezing point varies somewhat with concentration, in some cases this variation is very marked. Beckmann (Z P C 2, 742) recommends that a series of observations should be made, concentration varying so that the lowering of freezing point may range from c 2° to c 2°. If possible, observations should be made with solutions in different solvents, care being taken to select solvents which do not react chemically, so far as is known, with the dissolved body, and the results should be checked by ob-

servations of the lowering of vapour pressure of some solvent produced by dissolving in it the substance whose molecular weight is being determined (v infra)

To sum up this part of the subject Known weights of the substance, the molecular weight of which is to be determined, are dissolved in known weights of the solvent, so that the concentration of the solutions varies from, say, 1 tc 5 or 6 pc, the freezing point of each solution is determined. The freezing point of the solvent is determined. Two methods of calculation may then be adopted.—

(1) The lowering of freezing point, brought about by 1 g of the substance dissolved in 100 g of solvent, is calculated from each observation made, let this = A. The value of the constant expressing the molecular lowering of freezing point of the solvent by the class of bodies to which the substance under examination belongs is known,

let this be C Then $\frac{C}{A}$ gives approximately the

molecular weight of the substance

(11) The weight of the substance which would lower the freezing point of the solvent by 1° is calculated from each observation made, let this B Then $B \times C$ gives approximately the molecular weight (C has the same meaning as in (1))

The values found for mol w from the different observations are compared, if the differ ences are small, the mean is taken, if there are marked differences, experiments are made with other solvents. It may be that the substance undergoes dissociation in all solvents, and that, therefore, the method is inapplicable (v infra)

The molecular lowering of freezing point of the solvent may be calculated by the use of van't Hoff s formula $(t=01976 \ \frac{T'}{W})$, provided the

latent heat of fusion of the solvent is known, the value thus found should agree with the constant determined by experiment

The solvents commonly employed are water, benzene, phenol, and glacial acetic acid, naphthalene has also been used for some hydrocarbons, Eykman (Z P C 4,512) recommends urethane, phenyl propionic acid, the higher acids of the acetic series, stearin, and p toluidine Various modifications of Raoult's original apparatus have been devised, references to the papers in which the most important are described will be found at the end of this article

There are many apparent exceptions to Raoult's law, and therefore to van't Hoff's law of osmotic pressure These exceptions are explained by the hypothesis, put into definite form by Arrhenius ($Z \hat{P} C 1, 631$), that bodies whose behaviour is not directly expressed by these laws are partially dissociated in solution again there is a marked analogy between gases and dilute solutions, as the pressure of the vapour obtained by heating ammonium chloride is greater than the pressure calculated by Avogadro's law, on the assumption that the vapour consists of molecules of NH Cl, but as the observed pressure agrees with the calculated pressure when it is assumed that the vapour consists of equal numbers of molecules of NH, and HCl, so the apparently abnormal osmotic pressures of many solutions are brought into agree ment with van't Hoff's law by assuming that the bodies in these solutions are more or less dissociated into simpler molecules If the molecular weight of a substance, as determined by observations of freezing points, apparently decreases as dilution increases, it is likely that the substance is dissociated in the solution, and that the amount of dissociation increases as the quantity of solvent is increased Substances may undergo dissociation in one solvent and not in another (for several carefully worked out examples, v Beckmann, Z P C 2,715) Those sub stances, solutions of which show osmotic pressures agreeing with those calculated by van't Hoff's law from observations of the lowering of freezing-points of the solutions, are generally, if not always, non electrolytes The ap parent exceptions to the law of van't Hoff occur chiefly, if not wholly, among electrolytes dissociation-hypothesis of Arrhenius regards such electrolytes as more or less dissociated into their ions when they are dissolved in water great deal of work has been done in developing and applying the hypothesis of electrolytic dis sociation, an account of this work, and of the chief results, will be found in the article Physi CAL METHODS, section Electrical methods

Raoult has found that in many cases the lowerings of vapour pressure produced by dissolving a comparatively non volatile substance in a considerably more volatile liquid is related to the number of molecules of the dissolved body in 100 molecules of the solvent, provided the solution be very dilute (Z P C 2, 353) Arrhenius has shown that this generalisation made by Raoult can be deduced from van't Hoff's law of osmotic pressures (Z P C 3, 115) The gene ralisation has been placed on a thermodynamical basis by van't Hoff (Z P C 1, 493) and Planck (Z P C 1, 577) The law may be put in the following form At any specified temperature the ratio of lowering of vapour-pressure of a solvent, produced by dissolving a non-volatile body in it, to the vapour-pressure of the dissolved body to the total number of molecules of the dissolved body to the total number of molecules in the solution Let p = vapour pressure of solvent, p = p' = observed lowering of vapour pressure, W = weight of dissolved body, W - weight of solvent, m = molecular weight of dissolved body, and m' = molecular weight of solvent; then

$$p-p' \quad p = \frac{W}{m} \quad \frac{W}{m} + \frac{W'}{m'}.$$

If W, W', p, p', and m' are known, m can be found Suppose a grams of the substance are dissolved in 100 g solvent, then.

$$m = \frac{m \ p \ a}{100 \ p - p'}$$

Among the solvents which have been used in applying this law to the determination of molecular weights are ether, alcohol, CS₂, and Hg For descriptions of apparatus, and some of the data obtained, v Bacult (Z P C 2, 353), Walker (Z P C 2, 602), Beckmann (Z P C 4, 532), Ramsay (who determined mol w of several metals by using Hg as solvent) (C J 55, 521)

Baoult and others have found that the rise

in the boiling point of a liquid caused by dissolving a non-volatile substance therein bears a simple relation to the molecular weight of the dissolved substance There is a constant which must be determined for each solvent which ex presses the rise of bp caused by solution of I gram molecule of substance in 100 grams of solvent, for ether this constant is 21° (Beck mann, Z P C 3, 603) It is necessary then to find the weight of substance which, dissolved in 100 g ether, raises the b p 1°, the product of this weight multiplied by 21 gives, approxi mately, the molecular weight of the dissolved Thus Beckmann (lc) found that substance 2 153 g aniline dissolved in 100 g ether raised the bp of the ether 484°, therefore 4 45 g aniline would raise the bp 1°, but 4 45 × 21 = 934, the mol w of aniline is 93 Arrhenius contributes a note to Beckmann's paper (Z P C 4, 550) in which he shows, by thermodynamical reasoning, that the rise of boiling point (dT) of a solvent, caused by dissolving n gram molecules of another substance in 100 g of the solvent, is directly proportional to the quantity dissolved (n) and the square of the bp, and is indirectly proportional to the heat of vaporisation of 1 g of the liquid, W Put into an equation this state

ment reads thus
$$-dT = \frac{02T^2}{W}n$$
 This equation

is precisely similar to that found by van't Hoff (v p 419) for the molecular lowering of the freezing point of a solvent, only in the present case the quantities T and W depend upon the boiling point of the solvent A description of apparatus suited for applying the law of molecular raising of boiling point to molecular weight determinations will be found in Beckmann's paper, Z P C 4,543

References—Blagden, T 58, 277, de Coppet, A Ch [4] 23, 366, 25, 502, 26, 98, Rudorff, P 114, 63, 116, 55, 145, 599, Raoult, A Ch [5] 20, 217, 28, 133, [6] 2, 66, 93, 99, 115, 4, 401, 7, 289, 317, Z P C 2, 488, Eykman, Z P C 4, 497 (data bearing on question of series constants, influence of concentration, nature of solvent, &c)

The following memoirs bear chiefly on the similarities between the gaseous state and that of substances in dilute solutions —van't Hoff, Z P C 1, 481, 5, 175, 221, Arrhenius, ibid 1, 631, 2, 284, 491, Ostwald, ibid 2, 36, 270, Beckmann, ibid 2, 734, Nernst, ibid 2, 613, 4, 372, Planck, ibid 1, 577, 2, 343, Bredig, ibid 4, 444, Wiedemann, ibid 2, 241, and Ostwald's reply p 243, Pickering, C J 57, 331

The following memoirs are on the application of van't Hoff's law and Raoult's method to

The following memoirs are on the application of van't Hoff's law and Raoult's method to special compounds—von Klobukow, Z P C 3, 351, 476 (shows that CHI, and morphine do not give the anomalous results which Raoult supposed they did), Eykman, Z P C 2, 966 (morphine), Paterno a Nasim, B 21, 2153 (I), Loeb, Z P C 2, 606 (I), Beckmann, shod 5, 76 (I, P, S), Paterno, shod 4, 457, Sabanejeff, J R 1889 [1]515, abstract in B 28, [Ref] 37 (colloids); Brown a Morris, C J 53, 610, 55, 462 (carbo hydrates), Löw, B 21, 271, 22, 470 (sugars), von Klobukow, Z P C 5, 28 (sugars), Heycock a Neville, C J 55, 666, 57, 376, Kuster, Z. P. C 5, 601 (isomorphous mixtures)

The following memoirs deal with relations between osmotic pressures, lowering of vapour-pressure and of freezing-point, and raising of boiling point, of a solvent by substances dissolved therein —Airhenius, Z P C 3, 115, van't Hoff, ibid 1, 481, Planck, ibid 1, 577, van't Hoff a Reicher, ibid 3, 198, Guldberg, C R 70, 1349, Reckmann, Z P C 4, 532, Recult C R 110. Beckmann, Z P C 4, 532, Raoult, C R 110, 402, Raoult a Recoura, C R 110, 402

The following memoirs contain descriptions of apparatus — Auwers, B 21, 701, Hollemann, B 21, 860, Hentschel, Z P C 2, 306, Beckmann, ibid 2, 638, 4, 543 (raising b p), Eyk man, ibid 2, 964, 3, 113, 4, 497, Fabinyi, ibid 3, 38, von Klobukow, ibid 4, 10, Raoult, ibid 2, 353 (lowering vapour pressures), Walker, vent), Ramsay, C J 55, 621 (lowering vapour-pressures), Heycock a Neville, C J 55, 666 (using Hg as sol vent), Ramsay, C J 55, 521 (lowering vapourpressure of Hg) MMPM

MOLYBDATES Salts of molybdic acid v.

MOLYBDENUM, ACIDS OF, p 422

MOLYBDENUM Mo At. w 959 Mol w unknown S G 8 56 (Long, Am. S [2] 45, 131), 8 49 to 8 64 (Bucholz, Nucholson's J 20, 121) Does not melt in O-H flame at temp at which Pt melts (Debray, A 108, 250) SH 5°-15° 0659 (De la Rive a Marcet, A Ch [2] 75, 113) Emission spectrum (obtained by using electric spark) shows only a few lines, the most prominent in the blue and violet (v Thalen, A Ch [4] 18, 242) SVS c 113

Occurrence - Never uncombined The sulphide (molybdenite, or molybdenium glance), oxide (molybdenum ochre), molybdate of lead (wulfenite), and molybdate of cobalt (pateraite), occur in small quantities in certain localities Many iron ores contain small quantities of Mo compounds (Braun, Fr 6, 86, Wohler, Mineral analyse [Göttingen, 1861]) The residues from the copper smelting ovens at the Mansfeld works sometimes contain as much as 28 pc Mo (Heine, J pr 9, 176, cf Stromeyer, P 28, 551, Steinberg, J pr 18, 379, Genth J pr 37, 193, Steinacker, Ueber einige Molybdawerbin dungen [Gottingen, 1861] 22) An alloy of Mo and Pb, in plates 30 mm long, was found in Utah by Sillman (Am S [3] 6, 128) Accord ing to Lockyer (Pr 27, 279), Mo occurs in the

Scheele in 1778 (Opusc 1, 200) distinguished native Mo sulphide from galena In 1782, Hjehn obtained the metal from the sulphide (v Crell Ann for 1790, 1791, 1792, and 1794) historical account of this metal v Svanberg a Struve, J pr 44, 257 The name molybdenum was given from $\mu \omega \lambda' \beta \delta a \nu a$, or molybdena, used by Dioscorides and Pliny to designate galena and other lead compounds

Formation -1 By reducing MoO, by H, K or Na, C, or KCN -2 By reducing Mo chlorides by H at a high temperature —8 By reducing acid K molybdate by C —4 By electrolysing molten MoO₃, or (NH₄)₂MoO₄ in solution

Preparation—The starting-point is pure MoO₃ (v infra)—I MoO₃ is heated in a crucible in a stream of pure H (which must be passed over a long layer of red-hot Cu), the mass is transferred to a tube of unglazed porcelain, and very strongly heated in the H stream, finally the last traces of oxide are removed by gently

warming in a stream of dry HCl as long as a white wool like sublimate (MoO, 2HCl) is formed (Liechti a Kempe, A 169, 344) The metal in contact with the porcelain tube is not pure (Debray, C R 56, 732, cf Wöhler a von Uslar, A 94, 256, Rammelsberg, P 127, 284) -2 MoO. is mixed with C and heated in a graphite-crucible, in the O-H flame, the product always contains a few per cents of C (Debray, C R 46, 1098) -3 An intimate mixture of 1 pt MoO, and $1\frac{1}{2}$ pts KCN is placed in a crucible, the cover is luted on, the crucible is placed in another which is filled with C, and the whole is kept at white heat for 12 hours By this method Loughlin (Am S [2] 45, 131) obtained metal with 987

p c Mo
There are many methods for preparing MoO. from Mo ores Finely powdered molybdenite (MoS₂) is roasted in an open porcelain vessel, with frequent stirring, until SO₂ ceases to be evolved, Brunner (D P J 150, 672) recommends to mix the ore with its own weight of fine quartzsand, previously washed with HClAq, and to heat in a flat Pt dish, to incipient redness, till the residue is citron yellow when hot, and white when cold The roasted ore is treated with NH₃Aq, to the solution are added a few drops of NH, sulphide, the ppd CuS is removed, the filtrate is evaporated to dryness, the residue is dissolved in NH3Aq, and the solution is evaporated to the crystallisation point (Wohler) Svanberg a Struve (J pr 44, 264) add excess of K₂CO₃ to the ammoniatal solution of the roasted ore, separate ppd Al,O, evaporate to dryness, and strongly heat the residue in a Pt crucible, they treat with water, filter from CuO and Al2O2, evaporate to dryness, add S equal to double the weight of the residue, heat in a glass vessel on a sand bath to full redness till excess of S is burnt off, wash with warm water (the last washings containing a little K2CO3) as long as the washings are coloured, and until the MoS2 is perfectly black, and then roast the pure MoS. thus obtained, or oxidise it to MoO, by HNO, Aq Delffs (A 106, 376) decomposes molybdenite by HNO Aq Wittstein forms soluble sulphomolybdates by roasting with S, and decomposes by H SO Aq, finally roasting the sulphide to MoO3 (R P [2] 73, 155, cf Wicke, A 45, 378, Wohler, ibid p 374) Molybdenite may also be decomposed by calcining with alkali carbonates (v Christl, D P J 124, 398, Elbers, A 83, 219), or by the use of H.SO. (Elbers, lc)

Properties—As prepared by reducing the

chloride in H, Mo appears as dull silver-coloured, somewhat malleable, plates (Wöhler a von Uslar, A 94, 256) The metal obtained by reducing MoO, by Hat very high temperatures is lustrous, if the reduction is effected at lower temperatures, an ashen grey powder is obtained which becomes metal-like when rubbed The metal obtained by Debray, which contained 4-5 pc C, was silver white, and harder than topaz The SG of Mo 18 given by Loughlin (Am S [2] 45, 131) as 856, this metal contained 987 pc Mo bray (C R 46, 1098) gives S G 8 6 for the metal obtained by reducing MoO, by C, and containing

Mo, whether in powder or in pieces, is unchanged in ordinary air, when heated it becomes prown, then blue, then white, on the surface,

4-5 pc C

and at high temperatures it is burnt to MoO_s It is oxidised by fusion with KNO_s, or slowly by KOH, also by HNO_s, or Cl water, it burns when heated in steam, evolving H Mo is insol in HClAq, dilute H.SO_sAq, and HFAq, it is not acted on by KOHAq Mo combines directly with O, Cl, and Br, but not with I The metal is infusible at white heat (Debray, A 108, 250)

The atomic weight of Mo has been determined (1) by analysing, and determining V D of MoCl₃ (Liechti a Kempe, A 169, 344, Debray, C R 66, 732), (2) by determining S H of₂Mo (De la Rive a Marcet, A Ch [2] 75, 113), (3) by determining Cl in MoO₂Cl₂ (H Rose, P 40, 400, Svanberg a Struve, A 68, 209), (4) by synthesis of Ag₂MoO₄ (Debray, C R 66, 732), (5) by analyses of MoCl₂ and MoCl₄ (L a K, A 169, 344, cf L Meyer, ibid p 360), (6) by reducing MoO₂ in H (S a S, J pr 44, 301, Dumas, A Ch [3] 55, 143, Debray, C R 66, 732, Rammelsberg, B 10, 1776), (7) by oxidising MoS₂ to MoO₂ (S a S, A 68, 209), (8) by conversion of MoCl₄ and MoCl₄ to MoS₂ (L a K, A 169, 344, cf Meyer, ibid p 360) The atom of Mo is pentavalent in the gaseous mole cule MoCl₄

Mo is probably both metallic and non-metallic in its chemical relations. Few, if any, definite salts are known obtained by replacing the H of acids by Mo, but Mo₂O₃ and MoO₂ seem to dissolve in acids without evolution of O. The oxide MoO₃ is an anhydride, molybdic acid, H₂MoO₃, and molybdates, besides tri tetra n molybdates, are known MoO₃ also combines with some other anhydrides to form complex bodies which react as acids, e g

Pooles which react as acids, eg P₂O₅ 20MoO₅ 38H₂O, SiO₂ 12MoO₅ 26H₂O MoS₃ reacts as an acidic sulphide, forming sulphosalts M₂MoS₄ Several haloid compounds, and many oxyhaloid compounds, of Mo are known Mo is closely related to Cr, W, and U, and is less closely related to S, Se, and Te Mo occurs in Group VI series 6, the following table exhibits the position of Mo relatively to the other members of the group

Even series -

(v Chromium group of elements, vol 11 p 168, of Classification, vol 11 p 207)

Reactions—1 Heated in air or oxygen, Mo is burnt to oxide, if the temperature is sufficiently high, MoO₃ is formed—2 Oxidised, to MoO₃, by molten nitre, and slowly by molten potash—3 Heated in steam, blue oxide (? Mo₃O₃), and then MoO₃, is formed—4 Pulverulent Mo is oxidised by rubbing with silver oxide, or mercuric oxide 5 Oxidised by nitric acid, conc hot sulphuric acid, or chlorine water—6 Mo does not dissolve

o Ordineed by native acid, cone hot suppaired acid, or chloring water —6 Mo does not dissolve in hydrochloric, hydrofluoric, nor dilute sulphuric, acid, nor does it react with potash solution

Combinations —1 Mo combines with chlor

Combinations —1 Mo combines with chlor one to form MoCl₃, and with bromine to form MoBr₄ it does not combine directly with I—2 Heated in oxygen, Mo forms oxides, MoO₃ being the final product of the combination

Detection and Estimation -The greater

number of the Mo compounds, including most of the molybdates of the alkaline earths and heavy metals, are insol in water Lower oxides, and also the sulphides, produce MoO, when heated in air, MoO, readily dissolves in alkali solutions Insol molybdates are brought into soluble forms by fusion with alkali carbonates All Mo compounds may be changed to soluble alkalı sulphomolybdates by fusion with Na CO, and S Phosphomolybdates are readily soluble ın NH3Aq Mo compounds impart a yellow colour to the borax bead when heated in the oxidising flame, the colour disappears on cooling, in the reducing flame, they give a dark brown colour, the bead is opaque if excess of Mo com pound is present. They give a clear green microcosmic salt bead in the reducing flame, and in the oxidising flame a bead which is greenish when hot and colourless when cold In solution, Mo compounds give a brown black pp with H_2S , soluble in NH₄ sulphide, solutions of molybdates give blue coloured compounds by the action of reducing agents. When MoO, or a molybdate is evaporated with conc H₂SO₄, and then allowed to cool, the acid be comes deep blue in colour, this reaction dis tinguishes molybdates from tungstates, the blue colour does not appear if antimonic or stannic salts are present, unless the substance has been wetted with a few drops of phospholic acid, and evaporated to dryness, before addition of H₂SO₄ (Schönn, Fr 8, 379, Maschke, Fr 12, 383) If Zn is put into solution of a molybdate, a few drops of conc KCNSAq are added, and then enough HClAq or H.SO, Aq to cause slow evolution of H, a carmine red colour is produced, even with among part MoO, ether removes the

coloured compound (Braun, Fr 2, 36) Liquids containing molybdates yield deep red solutions (sulphomolybdates) by boiling with yellow NH, sulphide (Braun, Fr 6, 86)

Mois estimated (1) as metal by reducing in H (Rammelsberg, P 127, 281), (2) as MoO₄ by oxidising in air or by HNO₅Aq (v d Pfordten, B 15, 1927), (3) as PbMoO₄ (Chatard, B 4, 280, v also Ullik, A 144, 217), (4) by reduction with Zn and titration by means of standard KMnO₄Aq (Werncke, Fr 14, 1, v d Pfordten, B 15, 1927), (5) by the reaction of MoO₃ with an acidified solution of KI, whereby I is set free and is determined by standard Na₂S₂O₃Aq (Mauro a Danesi, Fr 20, 507)

Molybdenum, Acids of, and their salts The oxide MoO₃ is slightly sol in water, c 500 parts cold water dissolve 1 part MoO₃ solution reddens litmus Several hydrates of MoO_3 have been isolated MoO_3 $H_2O = H_2MoO_4$ was obtained by Ullik, and also by Vivier (v infra), the hydrates MoO₃ 2H₂O₂ 2MoO₃ H₂O, 4MoO₃ H₂O, 5MoO₃ H₂O, and 8MoO₃ H₂O, have also been prepared, some of these are soluble, and some are insoluble, in water Several series of salts are known, these salts may be represented as derived from hydrates of MoO3, in some cases the hypothetical hydrates have been isolated, and in other cases they have not been isolated Besides reacting as the anhydride of more than one acid, MoO, reacts with some oxides more acidic than itself to form com pounds, eg MoO, SO,, it also combines with certain acids—e g with HCl, H,PO, H,AsO, the compounds thus formed have acidic reactions and yield salts (v Antimono molybdates, ARSENO MOLYBDATES, PHOSPHO MOLYBDATES, p 425.

v also Molybdenum Trioxide, p 432)

MOLYBDIC ACIDS 1 H₂MoO₄ The normal hydrate MoO₂(H₂O₂, or hydroxide MoO₂(OH)₂, was obtained by Ullik, but only once, by mixing MgMoO, with an equivalent of HNO₃Aq and allowing to stand (A 153, 374) Vivier (C R Vivier (C R 106, 601) obtained this compound by allowing a solution of NH, molybdate in HNO, Aq to stand for some time, also by heating ordinary NH. molybdate solution with its own volume of water to 50°-60° for some days H₂MoO₄ forms a mass of minute needles, it is quite insol water

2 H2MO2O, The hydrate 2MoO, H2O (= MoO₂(OH)₂ MoO₃) was obtained by Ullik (A 144, 329) by the action of excess of H₂SO₄Aq on the Ba salt formed by adding BaCl2Aq to ordinary NH, molybdate solution, filtering, placing over H,SO, and drying the gum like residue over H2SO, for some months, or at 100° (Ullık, A 153, 373) H₂Mo₂O, is a gum like

amorphous solid, e sol water

3 H Mo₄O₁₃, and H₂Mo₆O₂, The 4MoO₃ H O (= MoO₂(OH)₂ 3MoO₃), and 8MoO₃ H O (= MoO₂(OH)₂ 7MoO₃) are The hydrates $8MoO_3 HO$ (= $MoO_2(OH)_2 7MoO_3$) are formed similarly to $2MoO_3 H_2O$, the drying being con ducted at 120°, and 160°-170°, respectively (U, These compounds are amorphous solids, e sol water Sabanejeff (J R 1889 [1] 515, abstract in B 23 (Ref) 87) obtained a colloidal form of H Mo₄O₁, sl sol water, by drying for some weeks over H_2 SO₄, the formula was deter mined by applying Raoult's law (cf Molfcular WEIGHTS, p 417) For other hydrates of MoO3, viz MoO, 2HO and 5MoO, HO, v HYDRATES OF MOLYBDENUM TRIOXIDE, p 432

Graham (C J 1864) obtained a soluble colloidal form of molybdic acid (he does not give the composition) by dialysing an aqueous solu tion of Na molybdate, to which excess of HClAq had been added, until the liquid in the dialyser was free from NaCl and HCl Graham describes the solution of molybdic acid as 'yellow, astrin gent to the taste, and to test paper, and possessed of much stability, it decomposed Na CO, with evolution of CO,, and became in sol when heated for some time with a strong

acid

Chloromolybdic H,MoO,Cl, acid $(=MoO(OH)_2Cl_2)$ (Molybdenum hydroxychloride) This compound is obtained by pass ing HCl over MoO, at 150°-200° (Debray, C R 46, 1101) It forms a loose, white, crystalline, mass, e sol water, sublimed unchanged in HCl

Thromolybdic acid and thromolybdates, v Molybdenum, Thioacids of, and THEIR SALTS, p 434

MOLYBDATES A great many molybdates are known, they are more or less closely related to the chromates The following classification is that given by Ullik (WAB60[2] 295), and now generally adopted R = divalent metal

Monomolybdates, RMoO, or RO MoO,, Dimolybdates, RMo,O, or RO 2MoO,, Trimolybdates, RMo,O, or RO 3MoO,, Tetramolybdates, RMo,O, or RO 4MoO, Octomolybdates, RMo,O, or RO 6MoO,, Detamolybdates, RMo,O, or RO 10MoO,, Tribasic heptamolybdates, R, Me,O, or or RO 3MO 7MoO,

There are a few molybdates which do not belong to any of these classes, eg 5Al₂O₂ 2MoO₂, and 2BaO 5MoO,

The alkalı monomolybdates are produced by dissolving MoO, xH2O, or MoO, in equivalent quantities of alkali, in solution or molten, they are easily sol in water The other salts of this series are generally insol in water, they are produced by ppn from the alkalı salts, or, in crystals by fusing Na2MoO, with NaCl and me tallic chlorides (Schultze, A 126, 55) alkalı dimolybdates are formed by fusing MoO, and alkalı carbonates in the proper proportion, or by the action of MoO, on molten alkali intrates (Ullik, A 144, 214) The trimolybdates are formed by boiling metallic carbonates with considerable excess of MoO, and water, filtering, and allowing to evaporate in the air salts are generally easily sol in hot water, but only slightly sol in cold water, many of them exist both in crystalline and amorphous forms, the amorphous varieties are readily sol in cold water (Ullik, A 144, 227, 153, 376) The tetra molybdates may be obtained by rapidly evaporating very small quantities of the solutions which yield trimolybdates when allowed to eva They form amorphous, brittle, porate slowly masses, which slowly decompose with formation of trimolybdates (Ullik, A 144, 321) lisable acid tetramolybdates are sometimes ob tained by adding a fair excess of acid to solutions of mono or dimolybdates, addition of a little acid to such solutions generally throws down trimolybdates Very few octo- or decamolybdates have been prepared

The following table presents the composition of the chief molybdates The small figures after the formulæ refer to the list of memoirs given after this table -

MOLYBDATES

Monomolybdates, RMoO, or RO MoO, $(NH_4)_2MoO_4$ (also infra, Mg salts) $5(NH_4)_2MoO_4$ Mn Mo_8O_{21} 12aq (22) (23, 27) BaMoO₄ (1, 23) BeMoO₄.BeO₂H₂ 6aq (24) CaMoO₄ (7) CoMoO, (1, 89) CoMoO, 2NH, aq (33) 3CuMoO₄ CuO, H₂ 4aq (11) Fe₂(MoO₄)₂ MoO₃ 7aq (34, Fe₂(MoO₄)₃ 2MoO₃ 16aq (25L₁,MoO₄ 2aq (17, 26) (20) MgMoO₄ 5aq (12, 21, 26) MgMoO₄ (NH₄)₂MoO₄ 2aq MgMoO₄ K₂MoO₄ 2aq (12) (12) MnMoO, (v supra, NH, salts, and infra, K salts) (1, 22, 39) Hg₂MoO₄ (29) NiMoO, 2NH, aq (1, 83) K,MoO, (also supra, Mg salts) (23, 26, 34, 26, MoO, Mn,Mo,O₂, 12aq (22) K,MoO, 2Na,MoO, 14aq (15, 26) 3Rb₂MoO₄ 4MoO₈ 4aq (26, 31) Ag₂MoO₄

derived from H,MoO₂ or H,O MoO₂

" H,Mo₂O₃ or H,O 2MoO₂

" hypothetical H,Mo₂O₃ or H,O 3MoO₂

" H,Mo₂O₁₂ or H,O 4MoO₃

" H,Mo₂O₁₃ or H,O 8MoO₃

" hypothetical H,Mo₁O₃ or H,O 10MoO₃

hypothetical H,Mo₂O₃ or 3H₂O 7MoO₃

```
Ag<sub>2</sub>MoO<sub>4</sub> 4NH<sub>3</sub> (85)
2Ag<sub>2</sub>MoO<sub>4</sub> 3MoO<sub>3</sub> (28)
Na<sub>2</sub>MoO<sub>4</sub> 2aq (also supra, K salts). (28, 28, 36° STMoO<sub>4</sub>. (1)
Tl<sub>2</sub>MoO<sub>4</sub> (26, 87)
STl<sub>3</sub>MoO<sub>4</sub> 8MoO<sub>8</sub> (87)
ZnMoO<sub>4</sub>. (1, 38)
```

Dimolybdates, RMo₂O₇ or RO 2MoO₃ or RMoO₄ MoO₅

Trimolybdates, RMo₃O₁₀ or RO 3MoO₃ or RMoO₄ 2MoO₂

Tetramolybdates, RMo₄O₁₅ or RO 4MoO₅ or RMoO₄ 3MoO₅.

(NH₄)₂Mo₄O₁₈ aq (25) BaH₂(Mo₄O₁₈)₂, 17aq (6) CaMo₄O₁₈ 9aq (7) CaH₂(Mo₄O₁₈)₂ 17aq (7) MgH₂(Mo₄O₁₈)₂ 19aq (12) KHMo₄O₁₈ 6aq (10) NaHMo₄O₁₈ 8aq (3) ZnMo₄O₁₈ 8aq (3)

Octomolybdates, RMo₀O₂₅ or RO 8MoO₂ or RMoO₄ 7MoO₅

Na₂Mo₈O₂₅ 4aq (1^a, 6) NaHMo₈O₂₅ 4aq (1^a, 6)

Decamolybdates, RMo₁₀O₂₁ or RO 10MoO, or RMoO₄ 9MoO₅

Na2Mo16O11 12aq (18, 6)

Tribasic heptamolybdates (sometimes called seven thirds molybdates), R₃Mo₂O₂₄ or 3RO 7MoO₂ or RMoO₄ 2RO 6MoO₅

(NH₄)₈Mo₇O₂₄ 4aq (ordinary ammonium molybdate) (16, 23, 26, 27)
Ba₈Mo₇O₂₄ 9aq (23, 31)
Mg₈Mo₇O₂₄ 20aq (12)
K₄Mo₇O₂₄ 4aq (23, 26)
Na₈Mo₇O₂₄ 22aq (18, 26, 36)

Molybdates not included in foregoing classes $5\text{Al}_2\text{O}_2\text{-2MoO}_3$ (18, 28) $4(\text{NH}_4)_2\text{O}.5\text{MoO}_3$ aq (80)

2BaO 5MoO, 6aq (23) CuO 2(NH₄)₂O 5MoO, 9aq (21) 7(NH₄)₂O 2Na₂O 21MoO₃ 15aq (26) 7(NH₄)₂O 3Na₂O 25MoO₄ 30aq (26)

For some other complex molybdates, v Bärwald, C C 1885 424 (Abstract in C J 50, 17)

Molyddates of Cd (1), Di (Frerichs a Smith, A 191, 355), La (F a F, lc p 365), Pb (23), and Manross, A 82, 358), and Sm (Clève, Bl [2] 43, 170), have also been prepared

Memor's where accounts of the molybdates will be found — (1) Schultze, A 126, 55 (1*) Ulhk, W A B 60 [2], 295 (2) Ulhk, A 144, 214 (3) Ibid id 144, 321 (4) Ibid id 144, 227, 153, 376 (5) Ibid id 144, 223 (6) Ibid id 144, 236 (7) Ibid id 144, 231 (8) Ibid id 144, 236 (9) Ibid id 144, 231 (10) Ibid id 144, 232 (20) Ibid id 144, 231 (20) Ibid id 144, 232 (20) Ibid id 144, 334 (11) Ibid id 144, 232, 233 (12) Ibid id 144, 334 (11) Ibid id 144, 233 (15) Ibid id 144, 339 (16) Ram melsberg, P 127, 298 (17) Ibid id 128, 311 (18) Struve, J pr 61, 449 (19) Ibid id 61, 457 (20) Ibid id 61, 459 (21) Ibid N Petersb Acad Bull 12,142 (22) Ibid J pr 61, 460 to 466 (23) Svanberg a Struve, J pr 44, 257 (24) Atterberg, J 1873 258 (25) Berlin, J pr 49, 445 (26) Delafontaine, J pr 95, 136 (27) Flückiger, P 86, 594, cf Werncke, Fr 14, 14 (28) Gentele, J pr 81, 414 (29) Hirzel, J 1852 419 (30) Jean, C R 78, 1436 (31) Jorgensen, Gm K 2 (22) 17 (32) Kammerer, J pr [2] 6, 358 (33) Sonnenschein, J pr 58, 486 (37) Flem ming, J 1868 250 (38) Mauro, B 14, 1379 (39) Coloriano, Bl [2] 50, 451 For an account of the crystalline forms of many molybdates v Zepharovich, W A B 58 [2], 111

To indicate the methods of preparation and properties of the molybdates, short descriptions are given of the NH, and Na salts, for the others, reference must be made to the original

Ammonium molybdates (1) Monomolybdate, (NH₄)2MoO4 Prepared by dissolving MoOs in excess of very conc NHsAq, and ppg by alcohol, obtained in small monoclinic crystals by spontaneous evaporation of the trimolybdate in conc NH, Aq Effloresces in air, with loss of NH₃, with water, forms an acid Forms double salts with MgMoO, and salt Mn.Mo₆O₂₁ (2) Dimolybdate, (NH₄)₂Mo₂O₇. Prepared by evaporating the mother liquor from which the monomoly bdate has separated, a white crystalline powder Forms double salts with date, (NH₁)₂Mo₂O₃, and Cr₂(Mo₂O₃)₃ (3) Trimoly b-date, (NH₁)₂Mo₂O₃ aq Prepared by slow decomposition of ordinary NH₄ molybdate solutions, at temperatures below 10° Lustrous needles, easily sol not waver, a double salt with Na₂Mo₂O₁₀ (4) Tetra-NH) Mo.O., aq Prepared by easily sol hot water, sl sol cold water Forms slowly decomposing solution of ordinary NH, molybdate by HClAq or HNO₃Aq, the solution eventually becomes filled with crystals of the tetra-salt, and the liquid is free from Mo (5) Tribasic heptamolybdate, (NH₄)₄Mo₂O₂₄ 4aq (=3(NH₄)₂O 7MoO₂ 4aq). This is the ordinary ammonrum molybdate used as a reagent for phosphoric acid, &c Crystallises from solution of MoO₂ in NH₂Aq, in large monoclinic prisms, unchanged in air The same salt crystallises with 12aq from the mother liquor

Treatment of ammonium molybdate residues Venator (Ar Ph [3] 23, 718) recommends to add enough FeCl, Aq to give a brownish colour to the solution, to ppt phosphoric acid by NH, Aq, to filter, and add BaCl. Aq whereby Ba molybdate and BaSO, are ppd The pp is thoroughly washed with hot water, and boiled for a long time with (NH,) 2SO, Aq, NH, molyb date separates from the filtrate on evaporation

Sodium molybdates (1) Monomolybdate, Na₂MoO₄ 2aq Prepared by fusing together equi valent quantities MoOs and Na, COs, dissolving in water, and evaporating, also by dissolving MoO₃ in Na₂CO₃Aq, also by neutralising the solution of any of the other Na salts by Na₂CO₃ Small lustrous tablets, sol water, solution has an alkaline reaction Solutions evaporated under 6° give a salt with 10aq, these crystals effloresce to the salt with 2aq Forms a double salt with K_MoO, (2) Dimolybdate, Na, Mo O Prepared by fusing together MoO, and Na, CO, in the proper proportion, and treating with a little cold water, also by adding MoO, to the equivalent quantity of molten NaNO, (only half of this is decom posed), and treating with cold water Small lustrous needles, sol with difficulty in water, hot or cold Melts at incipient redness, and crystallises on cooling An aqueous solution of this salt evaporated to a syrup yields crystals of Na Mo O aq, easily sol water (3) Trimolybdate, Na Mo₃O₁₀ 7aq Prepared by saturating warm Na2CO3Aq with MOO3, filtering, and allowing to evaporate spontaneously, also by adding excess of HNO3Aq to a conc solution of MoO3 in Na CO₂Aq, also by adding acetic acid to solution of Na No O 22aq, also by spontaneous evaporation of solution of NaHMo O₁, 8aq after addition of 1 or 2 formula weights of Na CO, A voluminous pp consisting of fine needles Small quantities of a hot conc solution of this salt give Na2Mo3O10 4aq on rapid evaporation, amorphous mass, easily sol water Forms a double salt with (NH₄) Mo₃O₁₀ (4) Tetra moly b-dates, (a) Normal salt, Na Mo₄O₁₈ baq Prepared by adding the proper quantity of HClAq to Na, MoO, Aq, and evapor ting, also by sponta neous evaporation of solution of NaHMo, O, 8aq, to which a little NaCl has been added Easily to which a little NaCl has been added sol hot water, sl sol cold water (b) Acid salt, NaHMo O 18 8aq Prepared by adding the proper quantity of HClAq to Na VoO, Aq Large monoclinic crystals, sol water, hot or cold Melts below redness (5) Octomolybdates, (a) Normal salt, Na MosO2, 4aq Prepared by digesting the acid salt with 1 formula weight Na CO3 in A white insol powder (b) Acid salt, NaHMo₂O₂, 4aq Prepared by adding excess of cone HNO₃Aq to boiling Na₂MoO₃Aq A white pp (6) Decamoly bdate, Na₂Mo₁₀O₂, 12aq Pre-A white pared by adding 2HClAq to Na MoO Aq, and evaporating on the steam bath Separates as a white, almost insol, crystalline powder (7) Tri-basic heptamolybdate, Na, Mo, O2, 22aq =3Na₂O 7MoO₂ 22aq) Prepared by dissolving MoO, in the calculated quantity of Na,CO, in water, also by mixing equivalent quantities of

Na₂Mo₂O₁₀ and Na₂CO₃ in solution, and evaporating, also from a solution of MoO₃ in MaOHAq or Na₂CO₂Aq, by adding HNO₂Aq as long as the pp of trimolybdate redissolves and until the liquid acquires an acid reaction Large, lustrous, monoclinic prisms, easily sol water, solution reacts acid Melts when warmed, and crystallises on cooling, the molten salt is insol water There are also several complex double sodium molybdates

Antimono-, arseno , fluo , phospho , silico-, Vanado , molybdates

Antimonoso-molybdates These salts are most simply regarded as compounds of Sb.O. with MoO. and basic oxides, they are obtained by boiling SbOCl with an acid molybdate solution (Gibbs, P Am A 21, 93)

Antimono molybdates Some of these salts, compounds of Sb₂O₃ with MoO₃ and basic oxides, are described by Gibbs (P Am A 21, 105)

are described by Gibbs (P Am A 21, 105)

Arsenoso molybdates Described by Gibbs (lc 21, 81) The former salts are obtained by boiling As,O, with cone solutions of acid molyb dates, the latter by oxidising the former in alkaline solution (For composition of fore going complex salts v abstracts of Gibbs' papers in C J Abstracts, 1886 426, 511, 1887 113, v also Pufahl, B 17, 217, Debray, C R 78, 1408, Struve, J pr 58, 493)

Arseno molybdic acids Compounds of H₂AsO₄ with MoO₁, v Sevberth, B 6, 391, Debray, C R 78, 1408, Struve, J pr 58, 493

Regarding the relations of the antimono and arseno molybdates to the phospho molybdates, v Phosphomolybdates, p 426

Fluo molybdates A number of salts are obtained by dissolving molybdates in HFAq and evaporating, others are formed by dissolving metallic oxides along with MoOs in HFAq and evaporating, other salts are produced by dis solving hydrated MoO2 along with metallic oxides in HFAq and evaporating, others by dissolving MoCl, in alkali fluorides These salts may be regarded as fluomolybdates, most of them belong to one of the series M¹ MoO₂F₄, M¹MoO₂F₃, or M¹₂MoOF₃, the first may be looked on as salts of the hypothetical acid H2MoO.F4, derived from H2MoO4, the second may be looked on as salts of the hypothetical acid HMoO F₃, derived from H₂Mo₂O₇, and the third as salts of the hypothetical acid H₂MoOF₅, derived from the hypothetical H.Mo.O The foregoing, and other, fluomolybdates may also be regarded as compounds of metallic fluorides with MoO₂F₂ and MoOF₃, respectively

Fluomonomolybdates, M¹2MoO.F₄ These salts, which may also be represented as 2MF MoO.F₁, are generally obtained by dissolving monomolybdates in HFAq, most of them are sol water, and crystallise well When carefully heated in air, many form molybdates, others give residues of metallic oxides (Delafontaine, J 1867 233) The chief fluomonomolybdates are the following (NH₄)2MOO.F₄ H₂O. triclinic tables, by adding slight excess of HFAq to a strongly ammoniacal solution of ordinary NH₄ molybdate, and evaporating, when heated, H₂O and HF are evolved and blue oxide of Mo remains (NH₄)2MOO.F₄, rhombic plates (Mauro, Mem R Acad des Lincer [4] 4, 481) CoMoO.F₄ 6H₂O, dark red efflorescent crystals,

obtained by dissolving equivalent weights of ever, exceed 6, in one case n=14 when R=Ag, CoO and MoO₃ in HFAq, and evaporating K₂MoO₄F₄H₂O, lustrous, triclinic crystals, obtained by dissolving K₂MoO₄ in HFAq, also by chief sub classes of these phospho molybdates adding KF to MoO₃ dissolved in HFAq. Other | are the following (Gibbs) —

 $\begin{array}{lll} 10\text{MoO}_2 & 2P_2O_3 & 5R_2O & xaq \;, & R=NH_1 \text{ and } K, x=7 \text{ and } 20 \\ 10\text{MoO}_2 & 2P_2O_3 & 6R_2O.xaq \;, & R=NH_4, \; K, \; Ag, \; x=14 \;, \; R=Na, \; x=28. \\ 32\text{MoO}_2 & 2P_2O_3 & 6R_2O & xaq \;, & R=NH_4, \; x=28 \end{array}$ $36MoO_3 2P_2O_5 2R_2O xaq$, R = Na, x undetermined, > 10 $86\text{MoO}_{3} 2\text{P}_{2}\text{O}_{5} 4\text{R}_{2}\text{O} x$ aq, $R = \text{Na}_{7} x$ 44MoO, 2P,O, 5R,O xaq, R=K, x=22 44MoO, 2P,O, 6R,O , R=NH, 44MoO, 2P,O, 6R,O xaq, R=NH,, x=18 and 24 $44\text{MoO}_{2} 2P_{2}O_{5} 6R_{2}O xaq$, R = K, x = 24

salts of this series are CdMoO,F, NiMoO,F, 6H,O, Rb₂MoO₂F₄H₂O, 2Na₂MoO₂F₄H₂O, Tl2MoO2F4 H2O, ZnMoO2F4 6H2O

M₁Mo₂O₄F, or Fluodimolybdates, Mi₂Mo₂O₃ Mi₂MoO₂F₃ (Delafontaine, J 1867 233) salts may also be represented as MF MoO₂F₂, they are obtained by dissolving dimolybdates in HFAq, or by treating the salts M₁₂MoO₂F₄ with HFAq The chief salts of this series are

NH₄MoO₂F₃ H₂O, and KMoO₂F₃ H₂O

Fluomolybdates other than the fore going The salts (NH,),MoO.F. (on MoO.F., 3NH,F) and (NH,),MoO.F. (NH,),MoO. (or MoO,F, 4NH,F (NH,),MoO,) are described by Mauro (Mem R Acad der Lincer [4] 4, 481) The same chemist (G 19, 179, v also B 15, 2509) describes the following salts — K, MoOF, H,O (or MoOF, 2KF H,O), obtained by dissolving MoCl₅, or MoO₂ xH₂O, in cone hot KFAq, and crystallising K₃Mo₃O₃F₁₄ H₂O (or 3MoOF₃ 5KF H₂O), by dissolving the pieceding salt in HFAq and evaporating (NH₄) MoOF₅ (or MoOF, 2NH₄F), by dissolving MoO₂ xH₂O in HFAq, adding NH, Aq till the green liquid becomes reddish, then adding HFAq till a green colour is produced again, and evaporating considerably at a moderate temperature (NH₄)₃Mo₃O₃F₁₄ H O (or 3MoOF₃ 5NH₄F H₂O), by dissolving the preceding salt in warm HFAq and evaporating

Phospho-molybdates The phospho molyb-

dates have been examined by Berzelius, Svanberg a Struve (*J pr* 44, 299), Debray (*Bl* [2] 5, 404), Rammelsberg (*B* 10, 1776), Finkener (*B* 11, 1638), and especially by Wolcott Gibbs (*P Am A* 17, 62, 18, 232, 21, 50) These salts are produced when phosphoric acid or a soluble phosphate is added to solution of a molybdate, with or without the presence of a free acid, also by fusing together phosphates and molybdates, by dissolving molybdates in soluble in water in phosphoric acid, by digest ing MoO₃ with an alkaline phosphate, and by treating mixtures of insoluble phosphates and molybdates with a dilute acid. The phosphomolybdates of the fixed alkaline bases may be dehydrated by careful heating, but MoO, is generally partially volatilised Solutions of these salts in NH, Aq are decomposed by H, S with formation of thio-molybdates

The phospho molybdates belong to the general form mMoO, 2P,O, nR,O raq, m is always an even number varying from 10 to 48, n varies from 2 to 6, and is generally = 6, n may, how-

The only phospho molybdic acid which has been isolated is 48MoO, 2PO, 6H2O 2aq, three hydrates are known in which x = 54, 92, and 100 (Gibbs)

The salts with 6R2O are regarded by Gibbs as normal salts, those with less than 6RO generally have acid reactions. To the ordinaryammonium phospho - molybdate - ob tained by adding excess of a mineral acid to a solution containing MoO,, PO, and an NH, salt — Gibbs assigns the composition 48MoO₃ 2P₂O₃ 5(NH₃) O H₂O 16aq (cf Svanberg a Struve, J pr 44, 291, Nutzinger, Pharmaccut Vierteljahresschrift, 4,549, Sonnenschein, J pr 53, 342, Lipowitz, P 109, 135, Seligsohn, J pr 67, 470, Hundeshagen, Fr 28, 141, 172, who says that when dried above 130° the salt is 12MoO, (NH,),PO,)

Gibbs (lc) describes four other series of phospho molybdates -

Metaphospho molybdates, mMoO_s nRPO_s pR O xaq

Hypophospho molybdates, mMoO, nH,PO, pR,O xaq

Phosphoroso molybdates,

mMoO, nH,PO, pR,O xaq

Phosphoroso phospho mMoO₃ nP₂O₃ n¹H₂PO₃ pR O r uq molybdates,

Metaphospho molybdates, represented by 10MoO, 4NH, PO, 3(NH,)2O 9aq and

14MoO, 3Ba(PO,), BaO 55aq are converted by acids into orthophospho molybdates (Gibbs, P Am A 21, 116)

Hypophospho molybdates are represented by 8MoO, 2H, PO, 2(NH,), O 2aq, this salt was obtained by mixing NaH, PO, Aq with solution of (NH4)8Mo,O24, and adding HClAq (G, P Am A

18, 232) Phosphoroso- molybdates are represented by 24MoO₈ 4H₃PO₈ 4(NH₄)₂O xaq, in which x=17and 25, obtained by adding H3PO,Aq (pro duced by adding water to PCl₃) to solution of $(NH_1)_0Mo_7O_{24}$ (G, P Am A 18, 237, 21, 89)

Phosphoroso phospho molybdates are represented by 72MoO, 3P,O, 2H,PO, 9(NH,),O 38aq, obtained by adding the product of the decomposition of PCl, by H,O to solution of 10MoO, 2P,O, 6(NH,),O 14aq (G, lc 21, 96)

Note — Pyrophospho-tungstates have been isolated, of the form $22WO_3$ $9P_2O_3$ pR_2O_5 , p=13, 18, and 20, an ortho-metaphospho tungstate has also been prepared, 22WO, 3(P,O, 3K,O) 6NaPO, 2K,O 2Na,O 42aq. Corresponding molybdates have not yet been isolated

Besides the foregoing phospho molybdates, representatives of phosphovanado- and phosphostanno-molybdates have been

prepared by Wolcott Gibbs

Phosphovanado molybdates are represented by 28MoO, 2P,O, 16V,O, 16(NH₄)₂O 100aq, and 48MoO, 2P₂O₅ V₂O₅ 7(NH₄)₂O 30aq These salts are obtained by digesting MoO, with solution of phosphovanadates, mP₂O₅ nV₂O₅ PR₂O₇ by heating solutions of vanado molybdates, $m\text{MoO}_3 \, n\text{V}_2\text{O}_3 \, p\text{R}_2\text{O}$, with alkaline phosphates in the presence of acid, and by heating V,O, with solution of an alkaline phospho molybdate (Gibbs, lc 18, 253)

Phosphostanno molybdates, the salt 16MoO, 3P.O, 4SnO, 3(NH4), O 28aq is obtained by pouring solution of SnCl, 2NH4Cl into a hot solution of the acid NH, phospho molybdate 10MoO₃ 2P₂O₅ 5(NH₄)₂O 7aq (G1bbs, lc 21, 120)

The arseno-molybdates already referred

to (p 425) belong to the series

mMoO3 nAs2O3 pR O xaq (arsenoso-compounds) where m = 6, 8, and 12, n = 3, 2, and 5, p = 2 and 3 (R = NH₄, $\frac{1}{2}$ Mn, $\frac{1}{2}$ Ba), and x = 6, 13, and 24 (Gibbs, P Am A 21, 81) The antimono molybdates (v p 425) belong to the series 17MoO₃ 3Sb₂O₃ 6(NH₃)₂O 21aq (antimonosocompounds), and the series

7MoO₃ 4Sb₂O₃ 5(NH₄)₂O 12aq (antimono com pounds) (Gibbs, P Am A 21, 93 a 105)

Silico-molybdates Alkalı molybdate solutions produce yellow pps when added to solu tions of alkali silicates in presence of HNO. (Knop, C C 1857 691, 861, Richter, D P J According to Parmentier (C R199, 183) 1231) these pps have the composition 13MoO, MI,SiO, xH O P obtained the acid 12MoO, H,SiO, 24H,O from the mercurous salt (C R 94, 213) This acid forms large yellow regular octahedra, melting at 45° and decompos ing below 100°, easily soluble in water and dilute acids, decomposed by excess of NH,Aq or alkalı carbonates with separation of silica Vanado molybdates These salts belong to

two series (Gibbs, P Am A 18, 240 a 264) Vanadio molybdates These salts are 6MoO, V2O, 2(NH4)2O 5aq, represented by

 16MoO_3 $2V_2O_4$ 5BaO 29aq, and 18MoO_3 V_2O_5 $8(\text{NH}_4)_2\text{O}$ 15aq, they are obtained by digesting V_2O_5 (free from VO) with solutions of alkaline molybdates, by heating together solutions of alkaline vanadates and molybdates especially in presence of acid, by boiling solu tions of alkaline vanadates or meta vanadates (e g NH, VO,) with MoO,, and by the decompo sition of phosphovanadomolybdates (v supra)

Vanadio-vanadico molybdates representatives of this series which have been isolated are 28MoO₄ VO₂ 4V₂O₃ 11(NH₄)₂O 20aq and 30MoO₄ 3VO₂ 2V₂O₃ 14BaO 48aq They are obtained by boiling VO2 and V2O5 with an acid molybdate, by the partial reduction of vanadio molybdates, and by digesting solutions of acid molybdates with solutions containing VO. and

Aluminos, chromico, ferrico, and mangano-molybdates have been obtained by Struve (Petersburg Acad Bull 12, 142) and Parmentier (C. R. 98, 389) These salts are

classed by Gibbs (P Am A 21, 121) as belong ing to the forms 10MoO, M,O, 2K,O 15aq, where M=Al,Cr,Fe, 12MoO, M,O, 6R,O xH,O, where M=Al,Cr,Fe, R=NH, K, or Na, and x is gene rally=20 to 22, and 16MoO, Mn,O, 5R,O 12aq

where R = NH, and K

Molybdenum, alloys of Mo alloys with eral metals With aluminium, a crystalline several metals powder consisting of microscopic rhombic prisms, approximating in composition to MoAl. is obtained by melting together 1 pt MoO, dis solved in HFAq and evaporated to dryness, 2 pts cryolite, 2 pts KCl NaCl, and 1 pt Al, and dissolving excess of Al from the regulus by NaOHAq (Wohler a Michel, A 115, 102) With iron, grey, hard, brittle, alloys are obtained by directly fusing the metals together, by reducing Fe₂O₃ 4MoO₃ in H at full red heat, an alloy of the composition Mo2Fe is obtained (Steinacker, Ueber einige Molybdänierbindungen [Göttingen, 1861]) Alloys with Cu, Au, Pt, and Ag have been described An alloy of Mo with lead was found in plates in Utah (Silliman, Am S [3] 6,

Molybdenum, bromides of Mo combines directly with Br to form three bromides MoBr, MoBr_s, and MoBr₄, no MoBr₅ corresponding with MoCl, has been isolated When Br is passed over strongly heated Mo, an oxybromide is formed, then a greenish grey sublimate of MoBr, near the heated part of the tube, the metal becomes yellow red and is eventually con verted into MoBr, between the MoBr, and MoBr, isolated lustrous black needles of MoBr, are formed The only halogen compound of Mo which has been gasified, and the mol w of which is known in the gaseous state, is MoCl,

MOLYBDENUM DIBROMIDE, MoBr₂(Mo₂Br₄Br)

(Molybdous bromide)

Preparation -1. By passing Br vapour, much diluted by CO_2 , over strongly heated Mo (Atterberg, J 1872 260) -2 By passing Br vapour over Mo at a moderate temperature, or over a heated mixture of MoO, and C, strongly heating the MoBr, thus produced, and treating the residue with water whereby unchanged Mo may be washed away (Blomstrand, J pr 82, 433)

Properties and Reactions -A golden yellow powder, unchanged by heat, insoluble in water and in all acids Concentrated alkali solutions produce alkali bromide and MoOxH₂O (Blomstrand, J pr 77, 91) Dilute alkali solutions pro duce alkalı bromide, and yellow solutions from which CO., ppts Mo₃Br₄(OH)₂8H₂O This compound, known as molybdenum bromohy droxide, is prepared by slowly adding CO2 to the solution of MoBr in KOHAq, or by adding acetic acid and then passing in CO, or by decomposing the solution when hot by NH,Cl (v Molybdenum bromohydroxide) The reaction of MoBr, with KOHAq points to the formula MosBr. Br. for the dibromide, the radicle MosBr, combines with acid radicles to form salts, v Molybdenum bromohydroxide, p 428

MOLIBDENUM TRIBROMIDE, MoBr. (Molybdomolybdic bromide) Obtained by passing Br va-pour overgently heated Mo, or by heating a mixture of MoO2 and C in Br vapour, any MoBr, and MoO.Br. formed are removed by heating in the stream of Br, as these compounds are more volatile than MoBr. (Blomstrand, J pr 82, 433). Forms a blackish green mass of small interlaced | oxybromide | a corresponding chlorohydroxide, Sublimes with difficulty, at bright red heat gives MoBr, and Br Unchanged by water, insoluble in conc HClAq and cold dilute HNO, Aq Slowly acted on by dilute alkali solutions, decomposed by boiling alkali solution with ppn of

black Mo.O. 3H.O (Blomstrand, lc)

MOLYBDENUM TETRABROMIDE, MoBr. (Molybdic bromide) Formed in small quantity by heating Mo in Br, appears as single, black, lustrous, needles Easily decomposed by heat to MoBr, and Br, the temperatures at which it is formed and decomposed being not very different Fusible and volatile, forming brown vapours Deliquescent, soluble in water, forming a brownyellow solution from which alkalis ppt rusty brown MoO, xH₂O (Blomstrand, J pr 82, 433) Molybdenum, bromochlorides of

Mo₃Br₄Cl₂ 3H₂O and Mo₃Cl₄Br₂ 3H₂O Produced by adding HClAq to a solution of MoBr₂ in KOHAq, and by adding HBrAq to MoCl₂ in KOHAq respectively, of Molybdenum bromo hydroxide, infra, and Molybdenum chlorohy-

droxide, p 430

Molybdenum, bromochlorohydroxide of MogCl4 BrOH xH2O, obtained by adding water to an alcoholic solution of Mo, Cl, Br, 3H,O, cf Molybdenum chlorohydrox de

Molybdenum, bromofluoride of Mo₃Br₄F₂ 3H₂O Produced by adding HFAq to solution of MoBr in kOHAq, of Molybdenum bromohyd oxide

Molybdenum, bromohydioxide of

Mo₈Br₄(OH)₂ Prepared by dissolving MoBr₂ in KOHAq, and passing in CO₂ or adding acetic acid, or by adding NH,Cl to a hot solution of MoBr. in KOHAq (Blomstrand, J m 82, 433, cf Atterberg, J 1872 260) The yellow crystalline pp, consisting of Mo₂Br₄(OH)₂ 8H O, is dried at 100° or in vacuo over H₂SO₄ by placing the pp. over H₂SO, the dihydrate Mo₃Br, (OH), 2H₂O

18 produced

MosBr. (OH) 18 a red powder, sol in KOHAq, this solution probably contains Mo₂Br₄)OK) Addition of acids to this solution generally ppts a compound of the acid radicle with the group a compound of the acid radicie with the group Mo₃Br₄, thus HClAq ppts Mo₃Br₄ Cl₂ 3H₂O, HBrAq ppts Mo₃Br₄ Br₂ 3H₂O, HFAq ppts Mo₃Br₄ F₂ 3H₂O, and HIAq ppts the double compound (Mo₃Br₄ I₂)₂ Mo₃Br₄(OH)₂ 8H₂O H₂SO₄Aq ppts Mo₃Br₄ SO₄ 3H₂O K₂Cr₂O₇Aq ppts black Mo₃Br₄ CrO₄ 2H₂O Addition of NH₄ molybeta acid materials and acids and acids and acids. date and acetic acid ppts the molybdate Mo_Br, MoO, 2H,O H,PO,Aq, H,C,O,Aq, and HNO₃Aq also yield pps, that by HNO₃Aq dissolves in excess of the acid Acetic acid and CO2 reppt the hydroxide from its solutions in The haloid compounds of the radicle Mo,Br, are yellow solids insol in excess of the haloid acids, they are decomposed by boiling water giving $Mo_2Br_4(OH)_2 xH_2O$ The sulphate is yellow, and is sol in excess of H2SO, Aq, this solution gives no pp with AgNO, Aq, addition of HClAq ppts Mo, Br, Cl, 3H, O

The compound MO₂Br₄(OH)₂ 8H₂O might be represented as an oxybromide of Mo, viz as Mo,OBr, 9H₂O, but the production of but production Mo, Br, (OH) by drying the hydrate, and the re actions of this compound with acids, are better expressed by representing the compound as a compound of the radicle Mo₂Br, than as an

Mo₃Cl₄(OH)₂, exists (v p 430) Molybdenum, bromo-iodide of, Mo₃Br₄I₂ This compound is only known in combination with Mo,Br,(OH),, the compound has the composition (Mo,Br, L), Mo,Br,(OH), 8H,O, and is produced by adding HIAq to a solution of cf Molybdenum Mo₂Br₄(OH)₂ in KOHAq, bromohydroxide, supra

Molybdenum, chlorides of MoCl, is formed when Mo is heated in Cl free from O, by heating MoCl, in H, MoCl, is produced, and MoCl, pro duces MoCl₂ and MoCl₄ when heated in CO₂ The formula MoCl₅ represents the molecular composition of the gaseous pentachloride, the mol w of none of the other chlorides in the gaseous state has been determined

MOLYBDENUM DICHLORIDE MoCl₂(? Mo₂Cl₄ Cl₂)

(Molybdous chloride)

Formation -1 By heating MoCl, in an in different gas (Blomstrand, J pr 77, 95, Liechti a Kempe, A 169, 344) —2 By heating Mo with HgCl = 3 By carefully heating Mo in Cl largely diluted with CO2

Preparation - MoCl,, as pure as possible, is placed in several porcelain boats, which are heated to dull redness in a glass tube, while a slow stream of perfectly day CO2, free from an, is passed through the tube, the contents of the

first boat are not quite pure MoCl2, but may be purified by gently warming with very dilute HNO₈Aq (Liechti a Kempe, A 169, 344)

Properties and Reactions -An amorphous dull yellow powder, unchanged in air, but when heated forms Mo₂O₃ and then MoO₃, volutilised with difficulty, insol water, dissolves in alcohol and ether (L a K, lc) Dissolves in HClAq and crystallises from this solution as MoCl H.O. MoCl₂ 2H₂O, or 2MoCl₂ 3H₂O (Blomstrand, J pr 77, 95, v infra, Combinations, No 1) Very slightly sol in HNO₃Aq, dissolved by H SO₄Aq, soluble in NH₃Aq, on boiling a brown powder containing N is ppd Decomposed by hot conc alkalı solutions with ppn of MoO xH₂O Dis solved by dilute alkali solutions to form a yellow liquid from which CO2 or dilute acetic acid ppts Mo₈Cl₄ (OH)₂ xH₂O, v infra Molybdenum chlorohydroxide This reaction suggests the formula Mo₂Cl₄ Cl₂ for the dichloride (cf Combinations, No 2), the radicle Mo₂Cl₄ combines with acid radicles to form salts, v Molybdenum chlorohydroxide

Combinations -1 With water to form the

hydrates MoCl, H₂O, MoCl₂ 2H₂O, and 2MoCl₂ 3H₂O (or Mo₃Cl₄ Cl₂ 3H₂O, Mo₃Cl₄ Cl₂ 6H₂O, and (Mo₃Cl₄ Cl₂), 9H₂O) The first of these hydrates is formed by dissolving MoCl₂ in rather dilute HClAq and allowing to stand, it forms thin yellow plates, insol water The second hydrate is formed by warming a solution of MoCl₂ in HClAq on a water bath, or by slowly diluting a conc solution, it forms long thin prisms, sol water, alcohol, and ether Dilute solutions of this hydrate deposit Mo₂Cl₄(OH)₂ xH₂O The third hydrate is formed by dissolving MoCl₂ in hot HClAq and allowing to cool, it forms lustrous needles, insol water, decomposed by hot water, decomposed by heat with loss of H₂O, Cl, and HCl (Blomstrand, J pr 77, 95) -2 With the alkali halord salts to form compounds of the type 2MX Mo,Cl, X, 2H,O

where $M = NH_A$ or K, and X = OI, Br, or I (Blomstrand, lc) Obtained by adding excess of haloid icid, HX, to solutions of MoCl2 in KOHAq or These compounds NH₄OHAq, and evaporating ire decomposed by water, with solution of KX, or NH4X, and ppn of MosCl4X23H2O solutions of these compounds AgNO, Aq ppts only half of the halogen present, thus 4Br is ppd from Mo.Cl, Br. 2KBi, and 4Cl from Mo.Cl, Cl. 2KCl These compounds are not de-Mo.Cl. Cl. 2KCl These compounds are not de-composed by H₂S in presence of acids, nor by **K**₄FeCy₅Aq

MOLYBDENUM TRICHLORIDE, MoCl. (Molybdo-

molybdic chloride)

Formation -1 By passing vapour of MoCl. over heated Mo (Berzelius) -2 By heating MoCl, by means of an ordinary spirit lamp, in a stream of H (Blomstrand, J pr 71, 449) -8 By passing CO2 charged with MoCl, through a tube heated in one spot, MoCl, remains behind the heated place as a thick crystalline crust (Blom-

strand, lc)

Preparation -MoCl, is prepared in a hard glass tube, narrowed at intervals so as to form B or 4 divisions (v Molybdenum pentachloride, Preparation), the greater part of the MoCl₃ is in the second division, while a little is in the first division Pure dry H is passed through the tube for some time, the second division of the tube is then heated until the MoCl, begins to sublime into the third division, the temperature of the third division is kept at 250°, at which temperature reduction to MoCl₂ proceeds When reduction is complete (known by the change of colour of black MoCl, into red MoCl,), the H is replaced by a stream of dry CO2, and the small quantity of MoCl, in the first division of the tube is sublimed over the MoCl, which is not yet quite pure (Liechti a Kempe, A 169, 344)

Properties and Reactions -A dark brownish red solid, resembling amorphous P Unchanged Heated in a tube drawn to a fine opening, MoCl, forms as a red crystalline sublimate, heated in air, gives a white woolly sublimate, then brownish red, and finally dark blue, vapours, while impure MoCl, remains (L a K, lc) Decomposes at red heat into MoCl₂ and MoCl₄ Insol water and HClAq, sol in hot HNO, Aq, also in conc H.SO, forming a deep blue liquid (L a K, lc) Decomposed by boiling water, also by KOHAq or NaOHAq, with ppn Mo₂O₃ 8H₂O, warm NH₃Aq produces a brown powder which contains N A compound of KCl with MoCl, was obtained by Berzelius by the action of K-amalgam on MoO2 dissolved in HClAq

MOLYBDENUM TETRACHLORIDE, MoCl. (Molyb-

dic chloride)

Preparation -MoCl, is placed in a porcelain boat and heated to dull redness, in a long tube of hard glass, in a very slow stream of pure, airfree, CO2, MoCl2 remains in the boat, and MoCl4 sublimes, and is carried forward some distance by the CO, (Liechti a Kempe, A 169, 344)

Properties -A brown semi crystalline solid, the vapour is intensely yellow Deliquescent, dissolves in water with hissing sound, the solution shows the reactions of salts of MoO. Somewhat sol in alcohol and ether, dissolved by H₂SO₄Aq with evolution of HCl, sol in conc

HNO, Aq

Reactions -1 Kept in contact with air, oxy chlorides are produced -2 Heated in air, MoO₂Cl₂ and MoO₃ 2HCl are formed —3 Heated in carbon dioxide, forms MoCl, and MoCl,, at a higher temperature the MoCl, is decomposed to MoCl, and MoCl.

Combinations.—1 With phosphorus pentachloude to form MoCl, 2PCl, a blush amorphous solid, obtained by the reaction of PCl, with MoCl, or MoO₂Cl₂ When this compound is heated, MoCl, PCl, is produced, a metal like lustrous solid, soluble in water to form a black liquid (Cronander, Bl [2] 19, 500) -2 With ammonium chloride to form 3MoCl, 2NH, Cl 6H, O, obtained by saturating NH, ClAq with MoCl, filtering from NH,Cl which separates, and allowing to crystallise forms green, deliquescent octahedra (Blomstrand, J pr 71, 449)

MOLYBDENUM PENTACHLORIDE, MoCl. Mol 272 75 VD at 350°=137 This chloride 272 75 was supposed by Berzehus, also by Blomstrand, to be tetrachloride, its composition was determined by Debray (C_R 66, 732)

Formation -1 By gently heating Mo or MoS₂ in Cl =2 By strongly heating in Cl a mixture of MoO₂ and C

Preparation -A tube of hard glass is narrowed at intervals so that 4 or 5 divisions are formed, a porcelain boat containing Mo is placed in the tube, and the Mo is heated in a stream of dry HCl so long as any white woolly sublimate of MoO, 2HCl is formed, this sublimate is driven out of the tube by warming in the stream of HCL After cooling, dry air free Cl is passed through the tube for at least an hour, to ensure the removal of every trace of air, and the Mo is then gently heated in the stream of Cl MoCl. is formed and deposited immediately in front of the porcelain boat, by careful heating while the stream of Cl passes, the MoCl, can be sublimed into the different divisions of the tube, each of which is then sealed off (Liechti a Kempe, A 169, 344)

Properties - A black, crystalline, lustrous mass, a shade of greenish colour indicates presence of oxychloride (L a K, lc) Melts at 194°, and boils at 268° (Debray, C R 66, 732) VD at $350^{\circ} = 137$ The vapour is dark red (Debray, Lc , Rieth, B 3, 668) May be sublimed unchanged in Cl or CO₂ Decomposed by heating in air with production of MoO₂Cl₂. Fumes in air, and deliquesces to a brown liquid Dissolves in water with decomposition, solution in a little water is brown, but becomes colourless on Sol in alcohol and ether, forming dilution green liquids Sol in H2SO, Aq and HNO, Aq

Reactions -1 Heated in air forms MoO, Cl. same change results by exposure to air -2 Reacts towards some organic compounds as a carrier of chlorine, e.g. CCl, and S₂Cl, are produced by passing Cl into CS₂ mixed with MoCl, (Aronheim, B 9, 1788) -3 Heated with ammonia or ammonium chloride produces compounds of Mo with N and

H (v Molybdenum, nitride of, p 430)

Combinations -With phosphoryl chloride, to form MoCl, POCl, , large dark green crystals, melting at 125°-127°, and boiling at 170° with separation into its constituents (Piutti, B 12, This compound is formed by heating PCl₅ with MoO₃, in the ratio 3PCl₅ MoO₃, to 170° in a sealed tube, pouring off the brown liquid from the crystals, washing the latter with CS,

and drying them in a stream of CO2

Molybdenum, chlorobromides of, Mo,Br,Cl_38H_O and Mo,Cl_Br_38H_O Produced by adding HClAq to a solution of MoBr₂ in KOHAq, and by adding HBrAq to a solution of MoCl₂ in KOHAq respectively (cf. Molybdenum bromohydroxide, p 428, and Molybdenum chlorohydroxide, infra)

Molybdenum, chlorobromohydroxide of

Mo.Cl. BrOH 2H,O, obtained by adding water to an alcoholic solution of Mo, Cl, Br, 2H,O (v next article)

Molybdenum, chlorohydroxide of

Mo₂Cl₄(OH)₂ 2H₂O Prepared by dissolving MoCl₂ in KOHAq, and neutralising by acetic acid, the octohydrate Mo₃Cl₄(OH)₂8H₂O 18 obtained by adding CO, or NH, Cl, in place of acetic acid The dihydrate a light yellow amorphous powder, insol water and alcohol, when freshly ppd and washed with cold water it dissolves readily in acids, but on boiling the solution in HNOsAq or H2SO4Aq the hydrate is reppd, and is now quite insoluble in acids. The octohydrate forms yellow lustrous crystals (Blomstrand, J pr 77, 95)

By adding HBrAq or HIAq to MoCl₂, or

Mo₂Cl₄(OH)₂ xH₂O, warming, and allowing to cool, the compounds Mo₃Cl₄Br₂3H₂O and Mo₃Cl₄I₅3H₂O are obtained, and by evaporating the mother liquor from the second of these, on the water bath, the compound Mo₃Cl₄ I₂·6H₂O 1s produced These haloid compounds of the radicle Mo₃Cl₄ are yellowish red crystals, soluble in alcohol, crystallisable from dilute HBrAq and HIAq respectively Addition of water to the alcoholic solution of Mo₃Cl₄Br₂3H₂O ppts

Mo₃Cl₄ BrOH 2H₂O (Blomstrand, lc)
The compounds Mo₃Cl₄(OH)₂ compounds MosCl4(OH)22HO and Mo₂Cl₄(OH)₂ 8H₂O might be represented as oxybromides of Mo, viz as Mo₃OCl₄3H₂O and Mo₃OCl₄9H₂O, but the reactions of these com pounds with HBrAq and HIAq, and the composition and properties of the salts 2KX Mo₃Cl₄ X₂ xH₂O (v Molybdenum dichlorede), are better expressed by representing them as hydrated hydroxides of the radicle Mo₂Cl₄ than as hydrated oxybromides a corresponding bromohydroxide, Mo, Br, (OH)2, exists (v p 428)

Molybdenum, chloro-iodides of $Mo_3Cl_4 I_2 xH_2O$, x=3 and 6 Obtained by add ing HIAq to MoCl2 or to Mo2Cl4(OH)2 xH2O (cf

preceding article)

Molybdenum, fluorides of No fluoride of Mo has been isolated Solutions of Mo₂O₃ xH₂O, MoO2.xH2O, and MoO3 xH2O, in HFAq may contain the corresponding fluorides (Berzelius) The first of these solutions is purple, on evaporation a purple coloured varnish is obtained, addition of KF, NH4F, or NaF, to this solution, and evapora tion, ppts rose coloured powders which may be double compounds of alkali fluoride and MoF, Solution of MoO, xH2O in HFAq is rose red, but goes colourless on addition of much HFAq, on evaporation it yields a crystalline solid which dissolves in water, KF ppts a reddish-brown solid Solution of MoO, in HFAq is colourless, on evaporation it yields a yellow syrup, addition of MoO. tion of KF produces 2KF MoO,F,H,O(=K,MoO,F,H,O), (cf. Fluo-

molybdates under Molybdates, p 425)

Molybdenum, fluobromide of Mo,Br,F, 3H,O, prepared by adding HFAq to solution of Mo,Br,(OH), or MoBr, in KOHAq of Molybdenum, bromohydroxide of, p 428
Molybdenum, haloid compounds of The

haloid compounds of Mo which have been iso lated are MoBr₂, MoBr₃, MoBr₄, MoCl₂, MoCl₃, MoCl₄, and MoCl₅, the three bromides are formed by the direct union of Mo and Br, MoCl, is produced by heating Mo in Cl, MoCl, is obtained by partial reduction (by H) of MoCl, and MoCl, and MoCl, are the products of the decomposition by heat of MoCl₃ The only one of these compounds whose molecular weight is known in the gaseous The reactions of the dibromide state is MoCl, and dichloride leave little doubt that the molecular formulæ of these compounds are not less than Mo_sX_e , these compounds react as Mo_3X_4 X_2 , the radicles Mo_3X_4 combine with acid radicles to form salts such as Mo_3Br_4 SO_4 and MO₈Cl₄Br₂ These radicles Mo₈X₄ also combine with alkali haloid compounds to form 2MY $Mo_3X_4Y_2xH_2O$ where M = alkalı metal and Y = halogen

No fluoride or iodide of Mo has been iso

lated with certainty

Molybdenum, hydroxides or hydrated oxides of, v Molybdenum, oxides of, p 431, also Molybdic acids, p 423

Molybdenum, hydroxychlorides of Mo(OH)2Cl2 v Chloromolybdic acid, p 423 Mo, Cl, (OH), v Molybdenum, chlorohydroxide

Molybdenum, hydroxybromide of,

Mo₃Br₄(OH)₂, v Molybdenum, bromohydroxide of, p 428 Molybdenum, 10dides of

None has been isolated with certainty A solution of MoO_xxH₂O in HIAq gives a crystalline solid on evaporation, this solid is sol water, on heating it gives MoO2 and HI (Berzelius)

Molybdenum, 10dobromide of Mo₃Br₄I₂ Known only in combination with Mo3Br4(OH), as (Mo₃Br₄I₂)₂ Mo₃Br₄(OH)₂ 8H O, which is produced by adding HIAq to a solution of Mo₂Br₄(OH)₂ in KOHAq, of Molybdenum, bromohydroxide of, p 428

Molybdenum, iodochloride of $Mo_3Cl_4I_2 xH_2O_1 x = 3$ and 6 Obtained by adding HIAq to MoCl₂ or Mo₃Cl₄(OH)₂ xH₂O,

Molybdenum, chlorohydroxide of, supra Molybdenum, nitride of Mo₃N₂, or (?) Mo₅N₃ A greyish black powder, obtained by passing dry NH, over MoCl, heated to full redness (Uhrlaub, P 101, 605) Heated to whiteness in NH3, Mo

is produced

COMPOUNDS OF MOLYBDENUM WITH NITROGEN AND HYDROGEN These compounds are produced by heating MoCl, or MoO, in NH, also by heating NH, Cl with MoCl, MoCl, melts when heated in dry NH₂, NH₄Ol volatilises, and on continued warming a blackish mass remains, which when powdered, quickly washed with water, and dried over H2SO4, has the composition Mo, N10H4 (Uhrlaub, P 101, 605) Wöhler (A 108, 258) regarded this compound as $4MoN_2Mo(NH_2)_2$ By heating to incipient redness, a body of the composition $Mo_2N_{10}H_4$ is produced (Uhrlaub, Lc) Both these compounds are black powders, heated in air they burn to MoO, and give off NH, with molten KOH they evolve NH, and with NaClOAq they evolve N (Uhrlaub, lc) By heating to a temperature slightly above that at which NH,Cl is sublimed, Tuttle obtained Mo, N, H, (A 101, These compounds are all reduced to Mo by very strongly heating in NH, According to Tuttle (l c), purple coloured to black crystals are obtained by heating MoOs to redness in NHs, and these crystals consist of MoO2, Mo nitride, and Mo amide

Molybdenum, oxides and hydrated oxides of The three oxides MoO, MoO, and MoO, have been isolated, there also exist one or more oxides with more O than Mo O, and less than MoO, a hydrate of the monoxide (MoO) was obtained by Blomstrand, but little is known concerning it The oxides Mo₂O₃ and MoO₂ are basic, they dissolve in acids to form salts, but little is known with certainty regaiding these salts MoO₃ 18 acidic, it is the anhydride of molybdic acid H MoO, and several other acidic hydrates of MoO3 are known, v Molybdenum, acids of, p MoO_s also combines with some acids, $e\bar{g}$ HCl, and acidic radicles, eg SO₃ The mol w of none of the oxides is known with certainty, as none has been gasified

HYDRAIFD MOLIBDOUS OXIDF, MOO THO By treating MoBr, with conc KOHAq, Blomstiand obtained a black hydrate of MoO (J pr 77, 91) This compound has been examined only slightly

MOLYBDENUM SESQUIONIDE, MO O, (Molybdomolybdic oxide) This oxide was regarded by Berzelius as the protoxide, its composition was determined correctly by Blomstrand (J pr 71,

454, cf Svanberg a Struve, J pr 41, 257)
Formation —1 By heating MoO₃ to redness for some time in a stream of H (S a S, lc) -2 By long continued digestion of MoO, with Zn and HClAq, the product oxidises readily in air (Berzelius) - 3 By decomposing MoCl₃ by KOHAq, washing the pp of Mo O3 3H O with cold water, pressing between paper, drying over H SO, and heating in vacuo (Blomstrand, J pr 71, 455)

Preparation - Mo O, 3H₂O is obtained by one of the following methods it is dried over H.SO, and heated to a moderate temperature, in iacuo, or out of contact with air (if heated in air it is oxidised to MoO) To obtain Mo2O3 3H O, HClAq 13 added to a conc solution of a molybdate till the pp which forms is redissolved, this solution is digested with Zn until the colour changes from blue to red brown and finally to black (Blomstrand, J pr 71, 455, Rammelsberg, P 127, 284, Weincke, Fr 14, 1, Pisani, Fr 4, 420, Macagno, B 8, 258, cf O von der Proidten, B 15, 1925) Addition of Addition of NH, Aq to this blick solution ppts Mn2O, 3H.O, care should be taken to ppt as little ZnO H.O as possible along with the Mo_2O_3 $3H_2O$ (the ZnO H_2O to come down when most of the The pp is washed with Mo₂O₃ 3H₂O is ppd) water containing a little HCl, to remove ZnO H2O, then with pure cold water (Blomstrand, lc), and is then pressed between paper Mo O, 3H,O 18 also obtained by reducing the HCl solution of a molybdate by K amalgam containing very little K, and then ppg by NH,Aq (Berzelius), also by adding NH,Aq to the solution obtained by boiling HClAq and Cu with PbMoO, (von Kobell, J pr. 41, 158, cf Hirzel, J 1850 309), or with MoO, Aq (Rammelsberg, P 127, 281)

Properties and Reactions -A black solid. As obtained by reducing MoO, with Zn and HClAq (v Formation No 2), Mo2O2 18 brassyellow and shows the same crystalline form as the MoO, from which it is prepared, this variety of Mo,O, oxidises in air more rapidly than the black variety obtained by heating the hydrate Heated in air, burns to MoO2. Insol acids

MOLYBDENUM HYDRATE OF SESQUIOXIDE Mo₂O₂ 3H₂O A black solid obtained as described under Molybdenum sesquioxide, Preparation The moist hydrate oxidises by exposure to air Dissolves slowly in acids to form purple solutions, which are opaque but become transparent and greyish brown when much diluted evaporation, dark grey or black, non crystal lisable, salts are obtained, these salts have not been examined at all satisfactorily, a phosphate, nitrate, borate, and several sulphates were obtained by Berzelius (P 6, 331, 369)

MoO₂ MOLYBDENUM DIOXIDE, (Molybdic oxide) By strongly heating NH, molybdate, in a closed crucible, Bucholz obtained a dark metallike mass which he regarded as Mo dioxide (Scher J 9, 485), but Uhrlaub (P 101, 605) and Tuttle (A 101, 285) showed that this sub-

stance contains N and H

Formation -1 By reducing MoO, or Hg. MoO. (H Rose, P 75, 319) by heating in H (Svanberg a Struve, J pr 44, 257, Rammelsberg, P 127, 281) -2 By melting Na, Mo, O₁₀ with $\frac{1}{3}$ its weight of Zn, added in small pieces, and repeatedly washing the cold mass first with warm conc kOHAq and then with warm HClAq, the product usually contains a little MoO₃ (Ullik, A 144, 227) -3 By strongly heating Na Mo₃O₁₀ in H and removing Na MoO, produced by very dilute KOHAq (S a S, lc) (? Na₂Mo₃O₁₀ + 2H₆ $= Na MoO_4 + 2HO + 2MoO_2$

Preparation - A mixture of 1 part MoO, 1 part K CO, and 1 part H3BO, is very strongly heated in a Pt crucible, the crystals of MoO found in the mass on cooling are washed with H₂O, then with dilute NH₂Aq, and then with di-

lute HClAq (Mauro a Panebianco, G 11, 501, cf Muthmann, A 238, 108)

Properties and Reactions—A daik brown powder, appearing somewhat purple in direct sunlight Obtained by fusing MoO, with K2CO, and H,BO, (v Preparation), MoO, forms copper red to grevish, metal like, very lustrous prisms, SG 6 44 at 10° (M a P, lc) Unacted on by alkalı solution, HClAq or HFAq, oxidised to MoO, by HNO, Aq, or by heating in air, heated in Cl forms MoO₂Cl₂. Slightly soluble in conc. H,SO, and cream of tartar solution

HYDRATE OF MOLYBDENUM DIOXIDE MoO_2xH_2O Obtained by adding NH, Aq to solution of MoCl, washing the pp with NH, ClAq, then with alcohol, pressing between paper, and drying in vacuo over H2SO. The solution of MoCl, may be prepared by digesting a cone so lution of MoO, in HClAq with powdered Mo or with Cu (in absence of air) till all is dissolved (Rammelsberg, P 127, 281, cf Hirzel, J 1850

MoO.xH2O is reddish-brown to nearly black, it closely resembles Fe₂O₃ 3H₂O Slightly solu ble in water, forming a reddish yellow liquid, which reddens litmus, and from which salts (e g. NH₄Cl) reppt the hydrate This solution gelalatinises after long standing, and dries to a brown black, insoluble, hydrate (Berzelius, Lehr-Moist MoO2.xH2O oxidises superficially m air, forming the blue oxide Heated in vacuo MoO₂ is produced MoO₂ xH₂O is insoluble in caustic alkali solution, but dissolves in alkaline carbonates and bicarbonates, these solutions reppt the hydrate on boiling, by standing in air molybdates are formed (Berzelius)

MoO2 xH2O dissolves in acids to form salts These salts are generally purple red to black, only a few are crystallisable, their solutions oxidise in air, alkalis ppt MoO₂ xH₂O from these solutions The same salts may be prepared by digesting MoO_3 and Mo with acids till the colour is reddish-brown Berzelius (P 4, 153, 6, 331, 369, 7, 261) prepared some of the salts of MoO₂, but they have not been examined satis factorily By mixing MoO₂ in HClAq with NH₄ molybdate, Rammelsberg obtained a crystalline salt (NH₄)₂O 2MoO₂4MoO₃9H₂O (P 127, 281)

MOLYBDENUM TRIOXIDE, MOO, (Molybdic anhydride) This oxide was obtained by Scheele in 1778 soon after he had distinguished native

Mo sulphide from galena

Occurrence -As molybdenum ochre in small

quantities in a few localities

Formation -1 By heating Mo, or any of the lower oxides, for some time in air -2 By pio longed heating of the lower oxides in steam (Regnault, A Ch 62, 356) -3 By roasting MoS_2 in air, or oxidising it by HNO₃Aq (v Molybdenum, Preparation, p 421)—4 From NH₄ molybdate, by evaporating with excess of HNO, and washing the residue with water (Brunner, $D\ P\ J\ 150,\,372)$, also by heating in thin layers spread out in a flat porcelain dish (Ullik, A 144, .205)

Preparation -Impure MoO, is dissolved in NH, Aq, H, PO, is removed by ppn with MgCl, Aq, the filtrate is evaporated, the crystals of NH4 molybdate which separate are heated with excess of HNO, Aq, and the residual MoO, is washed with water (For details as to preparation of MoOs from Mo ores v Molybdenum, Preparation,

Properties -A white, light, porous, solid, when thrown into water it separates into small, thin, lustrous, scales SG 439 at 21° (Schafa rık, J pr 90, 12) Strongly heated in an open vessel, sublimes in colourless, transparent, rhombic needles (Nordenskjöld, P 112, 160) Melts at red heat Soluble in 500 parts cold water (Bucholz, Scher J 9, 485), in 960 parts hot water (Hatchett, T 1795 323) The solution reddens litmus, tastes metallic (Wittstein, J 1860 159, Muller, J pr 80, 119) Soluble in acids, but scarcely soluble after being strongly heated Dissolves in alkali, alkaline carbonate, and cream of tartar solutions

Reactions -1 By heating in hydrogen MoO. is reduced to MoO2, Mo2O3, or Mo, according to the temperature employed -2 Reduced to Mo by treating with potassium or sodium -3 Reduced to Mo₂O₃ by digesting with hydrochloric acid and zinc or copper, &c, also by potassium-amalgam—4 Reduced to the blue oxide (v p 433) by a little hydrogen sulphide (excess of H.S produces black Mo sulphide), also by solution of sulphur droxide, hydrogen rodide solution, boiling hydrochloric acid, nitric oxide, or stannous

chloride -5 Heated with ammonia, compounds of Mo with N, and with N and H, are produced (v Molybdenum, nutride of, p 430 —6 Heated with sulphur, MoS₂ is produced —7 Oxy chlorides, along with molybdates, oxybromides, or oxyfluorides are formed by heating MoO, with metallic chlorides, bromides, or fluorides (Schulze, J pr [2] 21, 440) -8 Various reduction pro ducts result by heating with potassium volide (Schulze, lc) —9 Hydrogen chloride produces MOO₂ 2HOl (= MoO(OH) Cl₂, v Chloromolybduc acid, p 423) -10 Hydrofluoric acid probably produces MoO₂F₂ (v Molybdenum, ovyfluoride of, p 423) -11 Dissolves in fairly cone sul phuric acid, on evaporation, crystals of MoO, SO, separate (v infra, Combinations, No 3) Hot dilute H.SO.Aq, saturated with MoO, gelatinises on cooling—12 Reacts with alkalis to form molybdates, R.MoO., &c (v p 423)—13 Oxy chloride, MoO.Cl., is formed by heating in chlorine (H Rose, P 75, 319)—14 Oxychlorides are produced by heating with phosphorus tri or penta chloride (Michaelis, J 1871 249, Schiff, A 102, 116)

Combinations -1 With water to form various acidic hydrates (v Molybdic acids, p 423, also infra, Hydrates of molybdenum trioxide) -2 With hydrogen chloride to form MoO₈ 2HCl This compound is produced as a white, loose, sublimate, by heating MoO₃ in HCl to 150°-200°, it is easily soluble in water, and can be sublimed unchanged in HCl (Debray, C R 46, 1101) This compound may be regarded as an acid and called chloromolybdic acid, MoO(OH)2Cl2 (v p 423) -3 With sulphur trioxide to form MoO, SO, and with SO, and H₂O to form MoO, 3SO, 2H₂O MoO, SO, was obtained by Schultz Sellac (B'4, 14) by evaporating a solution of MoO₂ in fairly conc H₂SO₄, it forms lustrous, transparent, de liquescent crystals, which lose SO, when heated MoO, 3SO, 2H2O was obtained by Anderson (J B 22, 161) by adding excess of H SO, Aq to BaMoO₄, filtering, and evaporating —4 Com bines with the oxides of phosphorus, arsenic, antimony, vanadium, and silicon, in presence of basic oxides, to form salts of complex acids, v Anti mono, &c, molybdates, pp 425 et seq -5 With ammonium fluoride to form MoO, 2NH,F (? NH, salt of MoO(OH), F2), obtained in lustrous, light yellow, octahedral crystals, by adding NH3Aq to an aqueous solution of MoO,F, 3NH,F (this salt is obtained by evaporating a solution of NH, molybdate in excess of NH, FAq acidified by HFAq) (Mauro, Mem R Acad dei Lincer, [4] 4,

HYDRATES OF MOLYBDENUM TRIOXIDE compounds xMoO, yH2O have been isolated Four of these have been described under Molybdic acids (p 423), the remaining two are de scribed here

Monomolybdic dihydrate, MoO, 2H,O A yellow, crystalline, solid Slowly separates from a solution of 15 grs ordinary NH, molybdate in 1000 cc water mixed with 1000 cc HNO₂Aq S G 116, may be washed with cold water, sol in water and acids, solution reddens litmus and turns turmeric brown, cone HNO₂Aq separates MoO₂ (Millingk, *Gm -K* 2 [2],

Octomolybdic monohydrate, 8MoO, H₂O Obtained by ppg solution of or dinary NH4 molybdate by BaCl,Aq, decomposing the Ba salt by exactly the equivalent quantity of dilute boiling H₂SO₄Aq, filtering, evaporating over H₂SO₄ and drying at 160°-170° (Ullik, A 144, 329, 153, 373) Soluble in water

Oxides of molybdenum other than the di-, SESQUI AND TRI- OXIDE Several oxides appear to exist intermediate between MoO2 and MoO3, their compositions are not yet settled Some of them form hydrates of which some are soluble and some insoluble in water The substance known as 'blue oxide of molybdenum,' formed by the action of reducing agents on acid solu-

tions of MoO, is probably Mo,O,

References —Mo₃O₁₄, by heating lower oxides in air (Berzelius, P 6, 331, 369) Mo₂O₅, by heating (NH₄),0 2MoO₂ 4MoO₃ 9H₂O (Rammelsberg, P 127, 281) Mo₃O₈, by heating NH₄ molybdate with MoO₃ (Berlin, J pr 49, 447, NH₄), and the production of the state of Molyouace with Moo, (Berlin, a pr 30, 331, Whrlaub, P 101, 605), also by electrolysis of molten Moo, (Wöhler a Baff, A 110, 275) Mo₂O₁₁, by heating MoO, with KI (Schulze, J pr [2] 21, 440) Mo₂O₃ 3H₂O, by adding NH₄ molybdate or MoO, to MoO, in HClAq (Berzelius, Rammelsberg, lc) Regarding properties of the blue products obtained by reducing acid solutions of MoO3, v Schiff, A 120,47, Maschke, Fr 12, 384, Berzelius, Gm K 2 [2], 164, O von der Pfordten, B 15, 1925 Fairley (C J 31, 142) obtained indications of an oxide of Mo with more O than MoO₃, by adding H₂O Aq to MoO₃ dissolved in excess of alkali solution

Molybdenum, oxybromide of MoO.Br, Obtained by passing Br vapour over heated MoO₂, by melting MoO₃ with H₃BO₃, powdering, and then heating with KBr, by the reaction of MoO3 on many metallic bromides (Schulze, J pr [2] 21, 442) Yellow crystals, may be sublimed, deliquescent and soluble in water The compound MogBr4(OH), 8H O may be 1e presented as an oxybromide Mo,OBr, 9H2O, but is better regarded as hydrated bromohydroxide

(q v, p 428)

Molybdenum, oxychlorides of Many oxychlorides of Mo exist. They are produced by the reaction of Mo oxides with Cl, Mo chlorides with O, and PCl, and metallic chlorides with

MoO₃.

I Green oxychlorude Mo,O₈Cl₃₂, more probably MoOCl, (Blomstrand, J pr 71, 459, Putt bach, A 201, 123) By heating a mixture of Mo and MoO2 in air free Cl, and in many other Melts and sublimes below 100° Soluble in water Reduced by H at high temperatures, Puttbach (lc) describes Mo.O.Cl, as a product of this reduction

II Yellow white oxychloride MoO₂Cl By passing Cl over heated MoO2, or MoO3 (H Rose, P 75, 319), by heating Mo chlorides in presence of O (Blomstrand, lc), and in many other ways (v Schulze, J pr [2] 21, 441, Michaelis, J 1871 249, Schiff, A 102 216, Püttbach, Ic) Melts at a high temperature when heated under pressure, at ordinary pressure sublimes without melting, soluble in water and alcohol

III Violet oxychloride Mo₂O₁Cl₄, perhaps) Produced along MoOCl₂ (Blomstrand, l.c.) Produced along with the green oxychloride, than which it is much less easily volatilised Dark violet-red

erystals , deliquescent Vor. III

IV Brown oxychloride, Mo2O2Cl3 (Blom Produced, along with MoO2Cl2, by strand, lc) heating Mo.O. in dry Cl., purified by sublima-tion in H. Forms large dark brown crystals, melts easily, deliquescent and soluble in water Puttbach (lc) describes a brown oxychloride, Mo₂O₃Cl₄, obtained in the preparation of MoOCl₄, also a red oxychloride, Mo₃O₃Cl₃, obtained by heating the violet compound in CO₂

The compound Mo.Cl.(OH), 2H,O may be re presented as an oxychloride, Mo₃OCl₄ 3H₂O, but its reactions are more those of chlorohydroxide (q v) MoO, 2HCl, which might be represented as MoO₂Cl₂H₂O, is described as chloromolybdic

acid (q v)

Molybdenum, oxyfluoride of MoO₂F₂ duced by heating MoO, with metallic fluorides, as a blue-white amorphous sublimate (Schulze, J pr [2] 21, 442) A number of compounds are known which may be regarded as double compounds of MoO₂F₂ with alkali fluorides, others may be regarded as double compounds of MoOF, with alkalı fluorides, these are described as fluo molybdates (p. 425)

Molybdenum, phosphide of MosP, crystalline powder, SG 617, oxidised by heating in air, with cone HNO₂Aq forms H.PO₄ and MoO₂, heated in Cl forms MoCl, and PCl₅. reduces Cu solutions with ppn of Cu Produced by heating a mixture of 1 pt MoO₃ with 2 pts glacial phosphoric acid to a high temperature for some time, and washing with HClAq and then with NaOHAq (Wöhler a Rautenberg, A

109 374)

Molybdenum, salts of Little is known with certainty of the salts obtained by replacing H of oxyacids by Mo MoO2 and Mo2O3 dissolve in acids to form salts, but accurate analyses and description of those salts are lacking (v Molyb denum dioxide and sesquioxide, p 431) MoO SO, and combines with SO, to form MoO SO, and with HCl to form MoO, 2HCl, but those com pounds are probably rather acids than salts (v Molybdenum trioxide, p 432) The radicles MosBr, and MosCl, combine with certain acidic radicles to form salts (v Molybdenum bromo hydroxule, and chlorohydroxule, pp 428, 430)

Molybdenum, selenide of MoSe, Obtained, but not free from a greyish blue substance which is produced along with it, by saturating and NH, molybdate with H Se gas (Uelsmann, A 116, 125)

Molybdenum, sulphides of Three are known, MoS₂, MoS₃, and MoS₄. As none has been gasified the molecular weight of none is known with certainty MoS, and MoS, and probably also MoS2, are all acidic towards the alkali sulphides

MOLYBDENUM DISULPHIDE, MoS. Occurs native, as molybdenite, SG 4138 to 4569 Occura Prepared by heating to redness a mixture of 1 pt MoO, and 2 pts S, in a crucible, till excess of S is burnt off, and washing the residue with warm water as long as the washings are coloured (Svanberg a Struve, J pr 44, 264) According to Carnot (Bl [2] 32, 164) compounds of Mo generally yield MoS, when heated in a stream of dry H.S A black, lustrous powder, msol water, sol cone H2SO4, with evolution of SO2 and production of a blue liquid Forms MoO, when roasted in air, or heated with conc. FF

HNO.Aq, readily attacked by Cl. more slowly by Br, not acted on by aqueous alkalı but after fusion with alkali dissolves in water (? with formation of a thio-salt) Slowly reacts with steam at high temperatures (Regnault, A. Ch. 62, 385) Reduced to Mo by strongly heating in H (O von der Pfordten, B 17, 731)

(Thro-MOLYBDENUM TRISULPHIDE, MoS. molybdic anhydride) Obtained by passing H_2S into solution of a molybdate until decomposition is complete, i.e till all molybdate is changed to a thiomolybdate, adding dilute HClAq in slight excess, warming gently (Atterberg, J 1873 258), washing, and drying at a moderate temperature A black powder, red-brown when most Goes to MoS₂ when heated E sol alkalı sulphide solutions, slowly dissolved by alkali or alkali hydrosulphide solution, the solutions thus obtained contain thromolybdates, Mi2MoS, (v THIOMOLYBDIC ACIDS AND THEIR SALTS, infra) MoS, is reduced to Mo by heating in H (O von der Pfordten, B 17, 781)

MOLYBDENUM TETRASULPHIDE, MoS. pared by fusing a mixture of 2 pts MoO, and 1 pt K₂CO₃, powdering, boiling with water, filtering, diluting, saturating with H₂S, washing the pp with cold and then with hot water, then treating with HClAq, and heating the chocolate brown powder thus obtained to 140° in a stream of H₂S (Kruss, B 16, 2044) tained by heating MoS₂ to 100° in H₂S (K, *lc*) Also by boiling MoS₂ with K₂MoS₂Aq, washing the pp of MoS₂ and K₂MoS₃ with cold water, dissolving in boiling water, and adding acid to this solution (Berzelius) MoS4 is a cinnamonbrown powder, partially oxidised in moist air With basic sulphides forms perthiomolybdates M12MoS (v THIOMOLYBDIC ACIDS AND THEIR SALTS, infra)

Molybdenum, sulpho-acids of, v Molybdenum, thro acids of, and their salts

Molybdenum, thio- acids of, and their salts A number of molybdates are known in which O is partly or wholly replaced by S salts may be divided into two classes, those containing both O and S, these may be called oxy-thromolybdates, and those containing only S, these may be called thromolybdates latter salts are classed as thiomolybdates, de rived from MoS, and perthiomolybdates, derived from MoS. rived from MoS. The only this acid of Mo H.MoS.

PERTHIOMOLYBDIC ACID, H2MoS, obtained by adding a weak acid to K,MoS. (which separates during the preparation of MoS₄), washing with cold water, and drying over H₂SO₄ (Kruss, A 225, 1) Insol water, alcohol, and ether Sol warm NaOHAq, not acted on by NH2Aq, evolves H2S slowly when boiled with cone HClAq

OXY-MONOTHIOMOLYBDATES, MI, MOO, S Na salt is prepared by melting pure MoO, with dry Na₂CO₅ till CO₂ is all expelled, powdering the Na₂Mo₄O₁₀ thus obtained, dissolving in freshly-prepared NaHSAq, withdrawing the reddish heavy oil which separates, washing the crystals which are formed by allowing this oil to stand, with alcohol, ether, CS, and then again with alcohol and ether, and drying over H.SO.

(Krüss, A 225, 1). A hygroscopic salt, sol.

OXY-DITHIOMOLYBDATES, M12MoO2S2 The NH, salt is prepared, as golden-yellow needles, by passing H.S into NH, molybdate dissolved in NH_2Aq , at c 6° (Kruss, lc) The K salt is also described by Kruss (lc)

OXY - PYRODITHIOMOLYBDATES, M¹₂Mo₂O₄S₃ $(=2M_2M_0O_2S_2-M_2S)$ The salts of this series at present known are acid salts The NH, salt, NH,HMo,O,S,, is prepared, as a reddish-yellow pp, by adding NH,HS drop by drop to NH, molybdate at c 90°, filtering after addition of NH,Cl, washing with alcohol, and drying over Corresponding K and Na salts are de scribed by Kruss (l c)

TETRABASIC DIOXY DITHIOMOLYBDATES salt K_2O $3K_2S$ $2MoO_3$ $2MoS_3$ (= $K_8Mo_4S_9O_7$) was obtained by Kruss (lc) by adding alcohol to a solution of K2Mo3O10, repeatedly shaking the oil which forms with alcohol, separating the black flaky crystals from the yellow crystals and the brownish red powder, all of which are produced on standing, washing and drying

THIOMOLYBDATES, M¹,MoS₄ These salts are derived from the hypothetical thiomolybdic acid H MoS,, of which acid MoS, is the anhydride The soluble thiomolybdates are obtained by directly combining MoS, with basic sulphides, also by passing H,S into cone solutions of the corresponding molybdates, the insoluble thio molybdates are obtained by ppg salt solutions by soluble thiomolybdates The soluble thiomolybdates may generally be crystallised, the crystals show fluorescence, green in reflected, red in transmitted, light Solutions of these salts are red The thiomolybdates as a class are decomposed by heat, giving a mixture of sulphide of the basic metal and MoS2, the K salt is only partly decomposed at white heat Conc solutions are stable in presence of excess of MoS3, when diluted, and especially in presence of free alkalı, the solutions become turbid with formation of thiosulphates and thiomolybdates richer in S than the original salts Boiled in absence of air, the solutions evolve H2S and form MoS₂ and perthomolybdates, Mr. MoS₃ (Berzelius, P 7, 261, Kruss, A 225, 1, cf Bodenstab, J pr 78, 186)

Potassium thromolybdate, K2MoS4 pared by gradually heating, finally to a high temperature, a mixture of equal parts K2CO and S, with a little C, and a large excess of MoS2, dissolving in water, filtering, and crystallising (Hirzel, J 1850 319) Kruss (lc) ob tained this salt by dissolving 5 g K2MoO, in 16 cc water, adding 50 cc KOHAq, SG 146, and saturating with H₂S Red, rhombic, crystals, with greenish fluorescence Sol water,

acetic acid ppts K2Mo2S, The other thiomolybdates which have been

examined, more or less fully, are the salts of NH4, Ba, Cd, Ca, Ce, Cr, Co, Cu, Au, Fe, L1, Mg,

Mn, Hg, Ag, Na, Sr, Sn, U, and Zn

PERTHIOMOLYBDATES, MI2MOS. The soluble salts of this class are formed by boiling thiomolybdates M2MoS4 with MoS2, the insoluble salts by ppg salt solutions by soluble perthio-molybdates The perthiomolybdates are genemolybdates rally dark red . solutions of the alkali salts mye a pp of MoS_4 on addition of scids (Berzelius, P

Potassium perthiomolybdate, K2MoS, pared by saturating an acid K molybdate solution with H₂S (a mixture of K₂MoS, and MoS, is thus produced), boiling for some hours in a retort, cooling, collecting the pp of K, MoS, mixed with MoS₂, washing with water till the washings give a flocculent dark red pp on addition of HClAq, extracting with boiling water, and evaporating the solution Also by heating dilute K₂MoS, Aq with excess of MoS, nearly to 100° tall the liquid is nearly dry Also by reacting on MoS, with KHSAq A red mass, resembling an extract, on one occasion Berzelius obtained ruby-red crystalline granules Insol cold water, sol hot water Scarcely acted on by cold HClAq or KOHAq

The other perthiomolybdates examined, more or less fully, are the salts of NH4, Ba, B1, Ca,

Au, Fe, Hg, Ag, Na, Sr, and Sn

TRIBASIC DITHIOMOLYBDATES Krüss (A 225,1) obtained the salt K₄Mo₂S₃ (=3K₂S 2MoS₃ = K₂MoS₄ MoS₅ 2K₂S) by passing H₂S into K₂MoO₄Aq containing KOHAq, S G > 146 (cf Small red Potassium thiomolybdate, supra) dish orange rhombic crystals, sol water, insol alcohol and ether Decomposes slowly in air, giving K2MoS M M P M

MONARDA OIL The essential oil of Monarda punctata, which smells like thyme, contains thymol C₁₀H₁₄O [48°] and a terpene (Arppe, A

MÓNO This prefix is very seldom used in this dictionary Compounds whose names begin with mono are described under the name to

which mono has been prefixed

MORIN or MORIC ACID C13H8O6 aq (B a H), $C_{15}H_{10}O$, aq (from alcohol), $C_{15}H_{10}O$, 2aq (from water) (L) S 025 at 20°, 094 at 100° Occurs in old fustic (Morus tinctoria) to which it imparts its dyeing properties (Wagner, J pr 51, 82, Hlasiwetz a Pfaundler, J pr 90, 445, 94, 65, A 127, 852, Löwe, Z 1875, 117, Fr 14, 119, Benedikt a Hazura, M 5, 165, 667)

Preparation -1 Deposited as calcium salt from an infusion of the wood on cooling This deposit is extracted with alcohol, water is added to the alcoholic extract when calcium morate is ppd while maclurin remains in solution calcium salt is then decomposed by oxalic acid (Wagner) —2 The deposit is washed, heated with very dilute HClAq, freed from CaCl, by washing, and repeatedly dissolved in alcohol and

ppd by water (H a P, B a H)

Properties - Needles, v sl sol water, v sol alcohol, m sol ether, insol CS₂. The solutions are deep yellow Blackens at 300° H2SO, dissolves it, without change, forming a brownish yellow solution Its alkaline solutions are deep yellow Its solution does not ppt gela-It stains the skin yellow FeCl, colours the alcoholic solution deep olive green It reduces Fehling's solution on warming and am-moniacal AgNO₃ in the cold—Its alcoholic solution exhibits green fluorescence on the addition of an aluminium salt (Goppelsröder, J pr 101, 406, 104, 10, Z [2] 4, 154, 607) Morin yields resorcin on dry distillation

Reactions—1 Sodium-amalgam turns the

alkaline solution indigo blue and finally yellow.

the solution then containing phlorogluoin -2. Potash-fusion yields phloroglucin and resorcin. 3 Nitric acid in HOAe oxidises it to (4, 2, 1)-di-oxy-benzoic acid.—4 Bromins added to its alcoholic solution forms ethyl-tetra-bromomorin C₁₂H₂EtBr₄O, 4aq which is ppd. on adding water and melts at 135° Tin and HCl convert this ether into tetra-bromo-morin C₁₂H₂Br₄O, 2½aq which becomes anhydrous at 110° and then melts at 258° It dyes silk and wool yellow without a mordant

Salts $-KC_{12}H_{2}O_{4}$ yellow needles (from $K_{2}CO_{4}Aq)$ $-Ca(O_{12}H_{2}O_{4})_{2}$ yellow precipitate $Ba(C_{12}H_{2}O_{4})_{2}$ red-brown powder $-Zn(C_{12}H_{2}O_{4})_{2}$; lemon-yellow needles, insol water, sol alkalis -

PbC₁₃H₁₂O₂ egg yellow pp —Pb₂C₁₅H₁₆O₂ (L)
Morin sulphonic acid C₁₃H₂O₂ SO₂H 2aq Formed by heating morin with conc H2SO Golden brown powder, sl sol. cold, v sol hot, water —K,C₁₈H₈SO₁₀ ½aq golden needles — BaC₁₈H₈SO₁₀ Golden flocculent pp, converted by nitric acid into tri-nitro phloroglucin

Isomorın Formed by adding sodiumamalgam to an alcoholic solution of morin containing HCl until the solution is deep-purple, and then evaporating (H a P) Purple-red prisms When heated alone or in alcoholic solution, or more quickly by treatment with alkalis, it is reconverted into ordinary morin. Its solution mixed with dilute alum is dichroïc

Paramorin C₁₂H₈O₅ Obtained, together with a larger quantity of resorcin, by distilling morin mixed with sand (Benedikt, B 8, 606) Taste Yellowish, woolly needles (from ether) May be sublimed Reduces Fehling's n V sol hot water and ether (unlike solution morin) It dissolves unchanged in conc H2SO4 Alkalis form a yellow solution Unlike morin, its alcoholic solution is not ppd by Pb(OAc),

MORINDIN $C_{28}H_{30}O_{15}$ (A) [245°] (Stein) Extracted by alcohol from the root of various species of morinda used as a dye ('Suranji') in India (Anderson, Tr E 16 [6], 435, A 71, 216) Slender lustrous orange needles, when heated it gives off orange vapours which condense to red needles of morindone It is insol ether, v sl sol cold water and alcohol, sol aqueous KOH and conc H₂SO₄ forming reddish violet solutions Gives a red lake with alum, and a cobalt blue pp with baryta water Morindin resembles ruberythric acid C₂₂H₇₂O₁₄(Rochleder, Sitz B 7,806, Stenhouse, C J 17, 333) but differs from it in being insoluble in ether and in the behaviour of the red alkaline solution on boiling, for this becomes deep purple in the case of ruberythric acid, but does not change in that of morindin (Stein, J. pr. 97, 234, Thorpe a. Greenall, C. J. 51, 52, 53, 171)

Morindone C13H10O, Tri oxy methyl-anthraguinone (?) Formed together with glucose by boiling morindin with dilute mineral acids Red needles, resembling alizarin Insol water, v sol. alcohol and ether Its solution in potash is reddish-purple, but fades on standing (unlike alizarin) Conc H2SO4 gives a dark-blue solution (alizarin gives an orange solution) FeCl, gives a green colour On distillation with zinc-dust it yields methyl anthracene

MORINGIC ACID An acid supposed by Walter to exist as a glyceride in oil of ben (from Moringa aptera) but shown by Zaleski (B 7, 1018) to be cleïc acid

the aqueous extract of fustic has deposited morin, the filtrate be shaken with EtOAc, the acetic ether evaporated, and the residue dissolved in cold water and ppd by NaCl, brown amorphous moritannic acid separates first, followed by maclurin (Lowe, Fr 14, 127) V sol water The solution is ppd by albumen, gelatin, and alkaloids $FeCl_2$ gives a brownish-black pp Alcoholic lead acetate gives a pp $(C_{15}H_{12}O_{12}5PbO)$

MORPHINE or MORPHIA C₁,H₁₉NO₃ to CH(OH) CH—O—CH₂

CH₂CH₃(OH) CH—CH₂ OF

CH₂C(OH) O CH

CH₂C(OH) O CH

CH₃CH NMe CH₂

CH₃CH NMe CH₄

(?)

(Knorr, B 22, 1117) Mol w 285 [230°] (Hesse, Ph [3] 18, 801) S G 1 32 (Schröder, B 13, 1074) S 01 at 10°, 04 at 40°, 22 at 100° (Chastaing, Bl [2] 37, 477) S (absolute alcohol) 1 132 at 10 6°, 8 623 at 78° S (abcohol of 90 pc) 377 at 10 6°, 2 991 at 78° S (amyl alcohol) 268 at 11°, 2 247 at 78° (Florio, G 13, 496) S (ether) 023 at 10°(F) S (chloroform) 04 at 9 4°, 1 235 at 56°(F) S (amyl alcohol) 26 in the cold (Kubly, J 1866, 823) The solubility of crystallised morphine in boiling liquids is given by Prescott (Pk [3] 6, 404) as follows S (ether) 0163, S (chloroform) 023, S (amyl alcohol) 1, S (benzene) 0112 The solubility of amorphous morphine in boiling liquids is given by Prescott as S (ether) 0473, S (chloroform) 0506 The solubility of freshly ppd morphine in boiling solutions is given by Prescott as S (ether) 094, S (chloroform) 116, S (amyl alcohol) 11, S (benzene) 05 According to Burg (Fr 19, 222), the solubility of morphine in pure chloroform is 01, and in a mixture of 9 pts chloroform and 1 pt alcohol tis 9 [a]_D (in a 2 pc solution containing 2 mols NaOH) = -70 23° (Hesse, A 176, 190) [a]_D (in a solution of the hydrochloride) = -100 67°-1 14p, where p = percentage of salt present (Hesse, Grimbert, J Ph [5] 16, 295)

Occurs in opium, being known in an impure state as Magisterium opii in the seventeenth century, and was first isolated in 1816 by Sertimer (Gilb Ann 55, 61, 57, 192, 59, 50) Dott (Pr E 12, 189) found in a sample of opium that half the morphine was present as meconate and half as sulphate It also occurs in Eschscholtzia californica (Baudet a Adrian, G. C 1889, 197), and in hops

Preparation—1 Opium is macerated with Mater at 38°, the extract evaporated with CaCO_s to a small bulk, and then mixed with CaCl₂ The liquid is filtered from ppd calcium meconate and evaporated. It first deposits calcium meconate, and afterwards a mixture of the hydrochlorides of morphine and codeine. These crystals are dissolved in water and treated with ammonia, which ppts morphine, leaving codeine in solution (Robiquet a Gregory, A 5, 87, 7, 261)—2 The aqueous extract of opium is boiled with lime, and the filtrate boiled with NH₄Cl, which ppts morphine (Mohr, A 35, 120)

Properties —Small trimetric prisms (containing aq), v sl sol water, alcohol, and ether It has a very bitter taste, and is a powerful nar cotic poison. It dissolves readily to the extent of one equivalent in aqueous KOH, lime, baryta, and NaOH, but scarcely at all in ammonia and alkaline carbonates. It readily dissolves in acids. It is leworotatory. It loses its water of crystallisation at 100° (Dott, Ph. [3] 18, 701), and begins to sublime at 150° in dots (Blyth)

Reactions -1 Very readily oxidised, thus 014 pc of the base is sufficient to liberate iodine from iodic acid (Serullas, B J 11, 238) Morphine is oxidised by alkaline K₃FeCy₈ to pseudomorphine C₃₄H₃₈N₂O₆ (Hesse, A 235, 229), and the same substance is formed by the action of nitrous acid on morphine (Schutzenberger, A 108, 346, Bl 4, 176), and by allowing morphine to stand in aqueous NH, exposed to the air (Polstorff, B 13, 86) Morphine slowly reduces silver nitrate in the cold -2 On oxidation with alkaline KMnO, it yields an acid, apparently pyridine tricarboxylic acid (Barth a Weidel, M 4, 700) —3 Potash fusion yields protocatechnic acid (B a M) and methylamine (Wertheim, A 73, 208) Alcoholic potash at 180° forms methyl ethyl amine (Skraup a Wiegmann, M 10, 110) -4 Nitrous acid forms nitroso morphine, pseudomorphine, and a base $C_{17}H_{21}NO_5$ —5 Netric acid, diluted with $(1\frac{1}{2} \text{ mols of})$ water, forms at 100° an acid $C_{10}H_{2}NO_{2}$, which can be converted by conc HNO, into pierie acid, and which yields methylamine when heated with KOH (Chastaing, C R 94, 44, J Ph [5] 4, 338) -6 Converted into codeline by heating with NaOLt and MeI the yield being small owing to the formation of morphine methylo iodide (Grimaux, A Ch [5] 27, 273, Dott, Ph [3] 12, 1009) -7 On distil lation with zinc dust it yields pyridine, NH,, pyrrole, and a base which may be quinoline, as chief products, together with 4 p c of phenan threne and 1 pc of phenanthraquinoline (Gerichten a Schrötter, A 210, 396) —8 When evaporated with dilute H2SO, till white fumes appear, morphine yields a residue turned brown by alkalis Morphine (1 pt), heated with H_2SO . $(1\frac{1}{2} \text{ pts})$ and oxalic acid (2 pts), at 120° forms a product which, on diluting with water, leaves a yellowish white amorphous body undissolved This substance, C14H, NO4, is soluble in hot water and in alkalis. It turns green in air, and its alkaline solution turns red in air The red dened alkaline solution gives with HCl a blue pp, 'morphine blue,' C₁₃H₁₁NO₂, which can be crystallised from ether Malonic and succinic acids behave like oxalic acids, forming the com pounds C15H19NO5 and C16H21NO6 All these formulæ should perhaps be doubled (Chastaing a Barillot, C R 105, 941, 1012) -9 Heating with oxalic acid forms trimorphine -10 Heating with conc HCl yields apomorphine (Matthiessen a Wright, Pr 17, 455, 460), and the bases $C_{4}H_{25}ClN_0O_{45}$, $C_{44}H_{25}ClN_2O_{45}$, and $C_{135}H_{135}Cl_2N_4O_{24} - 11$ With $Cl\ CH_2\ OAc$ and H,SO, it gives an intense violet colour, and after dilution with water and addition of NH, an amor phous yellow base, possibly $CH_2(C_1, H_{18}NO_2)_2$, which gives a violet colour with H_2SO_4 (Grimaux, OR 93,217)—12 Aqueous allocan and SO, form C,H,N,O,C,H,NO,H,SO, (Pellizzan, A 248, 161).—13 Bleaching-powder, acting on a solution of morphine hydrochloride, forms C1, H16Cl2NO10,

a crystalline body (Mayer, B 4, 121)

Colour tests —1 Liberates iodine from iodic acid solution The brown colour is increased by adding ammonia (Lefert, J Ph [3] 40, 97). If a laver of very dilute ammonia be poured upon a very dilute solution of morphine containing iodic acid and starch, a brown ring below a blue ring will appear at the junction of the liquids (Dupré, C N 8, 267)—2 Chloride of gold colours the solution blue, being reduced to gold— 3 KMnO is reduced, becoming green -4 Ferric salts give a blue colour, destroyed by acids, by heat, and by alcohol (Robinet a Pelletier, A 5, 172) -5 FeCl₃, added to a previously heated solution of morphia in H₂SO₄, gives a deep red colour, changing to dirty green (Husemann, A 128, 305) According to Lindo (C N 37, 158), morphine, gently warmed with H2SO4 and FeCl2, gives an indigo blue colour -6 A solution of molybdic acid in conc H2SO4 gives, with solid morphine, a violet colour, changing through blue to dirty green (Frohde, Fr 5, 214) -7 A solution obtained by adding ammonia to cupric sulphate till the pp cupric hydrate is just re dissolved is coloured green by salts of morphine (Nadler, F_1 13, 235, Lindo, F_r 19, 359) — 8 Nitric acid gives an orange red colour, gra dually changing to yellow -9 H.SO, contain ing a little nitric acid, gives a violet red solution (Erdmann, A 120, 188, Husemann, A 128, 305) -10 When morphine is boiled with aqueous phosphorous or hypophosphorous acid, and conc HSO, is added, the liquid becomes reddish On now adding a little nitric acid the solution becomes vellowish, and on warming with copper it assumes a splendid blue colour (Dragendorff, J 1864, 727) -11 KClO, (free from chlorate), added to morphine mixed with H SO, gives a dark brown colour (Grove, Fr 13, 324, Siebold, ibid)—12 Conc H₂SO, fol lowed by water and some oxidising agent (todic acid, K₃FeCy₆, K₂Cr O, KNO₃, MnO₅, or PbO), best in the solid state, gives a deep red colour on gentle warming (Lindo, C N 36, 228, Dott, C N 36, 255)—13 A mixture of K₃FeCy₅, ferric chloride, and HCl is coloured blue This reagent may be used to detect morphine in quinine salts (Kieffer, A 103, 271, Hagei, Fr 12, 220, Armitage, Ph 18, 761) According to Hesse (Ph 18, 801), the blue colour is due to pseudomorphine, not to Prussian blue -14 Chlorine water and ammonia give a red colour in a 1 pc solution (Fluchiger, Ar Ph [3] 1, 117)—15 Aqueous K.Cr.O., gives a dirty brown pp (Plugge, Ar Pl. [3] 25, 793)—16 Conc H₂SO₄, containing a little K₂AsO₄, gives on warming a blue violet colour, changing to dark brown red Water turns this green, and chloroform on shaking with it becomes violet, while ether becomes violet red, the liquid below it being brown (Tattersall, C_N 41,63, Donath, pr [2] 33, 563) -17 H₂SO₄ and a little KClO, gives in the cold a grass green colour, the edge of the liquid being pale rose colour (Vitali, B 14, 1583)—18 A mixture of morphine (1 pt) and powdered sugar (7 pts) turns purple on addition of a drop of H₂SO₄, the mass gradually changing in colour through bluish green to yellow (Schneider, J 1872, 747)—19 If morphine is heated with H₂SO₄ at 200°, and the

mass poured into water, the liquid becomes blue If chloroform be shaken with this liquid it acquires a blue colour, while if ether be used the ethereal layer becomes purple (Jorisson, Fr 20, 422) -20 On warming morphine with H2SO4 and sodium phosphate a violet colour appears (Vulpius, Ar Ph [3] 25, 256)

Estimation in Opium - Opium (200 pts) 18 exhausted with warm water and the extract evaporated to a thin syrup, mixed with alcohol (40 pts of S G 82), ether (380 pts), and ammona (45 pts of S G 935) The mixture is occasionally shaken, and after 18 hours it is filtered and washed with alcohol-ether The pp is dried, digested with benzene, dried, and weighed After weighing the base may be titrated with standard HCl (Teschemacher a Smith, C N 57, 93, 103, 244, Fluckiger, J 1885, 1962, Ar Ph [3] 27, 721, Venturini, G 16, 239, Stillwell, Am 8, 307, R Williams, C N 57, 134)

Another method consists in exhausting 7 g of opium with 110 cc of water and 4 g of slaked lime 50 cc of the filtrate are mixed with 5 cc of 95 pc alcohol, 25 cc of ether, and 3 g of NH,Cl After standing for 12 hours the ether is filtered off, and another 10 cc of ether added. The entire liquid is then filtered and the morphine collected on the filter determined by direct weighing or by titration (Goebel, Chem Zeit The morphine may also be extracted 11,508) from the opium by baryta water and ppd by CO2 (Yon Perger, J. pr. [2] 29, 97) Indeed, a great many processes for estimating morphine in opium have, from time to time, been proposed (Guillermond, J. Ph. [3] 16, 17, [4] 6, 102, Riegel, Jahrb pr. Phann. 23, 202, Guibourt, J. Ph. [3] 41, 97, 177, F. Mayer, Am. J. Pharm. 25, 284, Pharm. 1873, 641. J Ph [3] 41, 97, 177, F Mayer, Am J Pharm.
35, 28, Arnold, Russ Zeit Pharm 1873, 641,
Lynn, Amer J Pharm [4] 6, 358, C J 34,
612, Flewy, J Ph [4] 6, 99, Schachtrupp, Fr
7, 284, 509, Merck, A 18, 79, 21, 202, 24, 46,
Stein, Ar Ph [2] 148, 150, C J 25, 180, J T
Miller, Ph [3] 2, 465, C J 25, 181, Reveil,
Monit Scient 13, 312, J 1871, 821, Kremel,
C C 1887, 1529, Adrian a Gallois, J Ph [5]
5, 193, Schillum, Ar Ph [3] 25, 18, Dott 15, 193, Schlikum, Ar Ph [3] 25, 13, Dott, Ph [3] 18, 82, Plugge, 4r Ph [3] 25, 343)

Methods for separating morphine from other alkaloids have been given by Dragendorff (Ph. [3] 7, 24), Hager (C C 1872, 727), Neubauer

(Fr 9, 134), and others

Salts —B'HCl3aq S 5 in the cold, 100 at 100° (Regnault, A Ch [2] 68, 131, A 26, 24), 4 at 15° (Hesse, A 179, 190) [a]_j = -94° in a 2 pc solution containing excess (10 mols) of Silky fibres (from water) -B'HCl (MeOH) 2 at 15° Minute prisms (from MeOH) The salt B'HCl 3aq is partially rendered anhydrous by solution in alcohol (Hesse, A 202, arous by solution in account (1888), 1811—1811—1814—1814, yellow curdy pp, m sol water (Liebig, A 26, 46) Decomposed by boiling water (O de Coninck, Bl [2] 45, 181) ing water (O de Connor, B [2] 40, 181)—
B',H,PtCl, 6aq (Hesse)—B'HCl(HgCl.),. Crystalline pp (Hinterberger, A 77, 201)—
B'ZnCl, 2aq—B'ZnCl, 7aq (Graffinghoff, Z 1865, 600)—B'HBr 2aq needles (Schmidt, B 10, 194)—B'HI 2aq long silky needles grouped in rosettes, sl sol cold water (Schmidt, B 10, 194)—B'HI 2ar, Chapper Ar. Bh (24, 890). 194) —B'HI 3aq (Bauer, Ar Ph [3] 5, 289) — B'HI aq hair like needles (Kunz, Ar Ph. [3]

26, 307) -B',I, crystalline mass (B) -B'HI, obtained by ppg a salt of morphine with iodine dissolved in HIAq Brown pp, sol KIAq, from which it crystallises in nearly black prisms, sol which it drystallises in nearly black prisms, solal alcohol and boiling ether (Bauer, Jörgensen, J pr [2] 2, 487, Z [2] 5, 673) — B'HHgI, crys-talline pp, m sol alcohol (Groves, C J 11, 97) —B' $_2$ H $_3$ SO $_4$ 5aq [a] $_{\rm D} = -100$ 47 — 96p m a ppc solution at 22 5° (Hesse) S 4 in the cold (Dott) —B'HClO $_4$ 2aq needles (Bödeker, A 71, 63) —B'HVO $_4$ (Ditte, A Ch [6] 13, 237) — B'HCVS $_{\rm Log}$ [1002] Needles (Dollfus, A, 65. B'HCys aq [100°] Needles (Dollius, 4.65, 214)—B'_HPtCy, groups of minute needles (Sohwarzenbach, C. C. 1860, 304)—*B'HOAc 8.50 in the cold (Dott) Tufts of needles, v. sol water, m. sol alcohol (Merck, 4.24, 48)— B'CH_Cl CO_H (Florio, J 1883, 1343) —
B'CH_Cl CO_H (Florio, J 1883, 1343) —
B'CHCl, CO_H jaq — B'CCl, CO_H ljaq —
Butyrate B'C,H₀O₂ S 14 at 12° (Decharme,
J 1863, 444) — Valerate B'C,H₀O₂ Large trimetric crystals (Pasteur, A Ch [3] 38, 455) 28 in the cold (Dott) —Lactate B'C3H6O3 monoclinic crystals S 10 at 13° (Decharme) -Trichloro-lactate B'C,Cl₂H₃O₃ 5aq (F) —
Oxalate B'₂H₂C₃O₄ aq prisms S 48 at 12°
(D) —Tartrates —B'₂C₄H₆O₄ 3aq Nodular groups of needles, efforescent at 20° (Arppe, J pr 3, 332) B'C,H,O, ½aq S 11 in the cold (Dott) $B'C_1H_4O_4\frac{1}{2}aq$ Tufts of long rectangular flattened prisms (A) —Mellitate B'_3C_1,H_4O_{12} minute needles (Karmrodt, A 81, 171) Phenyl acetate B'CH,Ph CO,H [92°] — Nitroprusside (Davy, Ph [3] 11, 756)

Metallic derivatives C1, H18KNO, 25aq Obtained in a crystalline state by evaporating a solution of morphine in KOHAq in a desiccator over H_3SO_4 (Chastaing, J Ph [5] 4, 19)—(C₁,H₁₈ KNO_3)₂ K_2CO_3 2aq — $Ba(C_1,H_{18}NO_3)_2$ 3aq white crystalline solid — $Ca(C_1,H_{18}NO_3)_2$ 5aq —

Ca(C17H17NO2), 2aq

(a) Acetyl derivative C17H18AcNO3 tained, together with the (B) modification, by boiling morphine (1 pt) with HOAc (2 pts) for several hours (Wright, C J 27, 1033, Beckett a Wright, C J 28, 315) Crystallises from ether, either with aq or in the anhydrous state Gives no colour with FeCl, —B'HCl3aq crystals, sl sol cold water -B'2H2PtCl6 amorphous -B'Etl laq crystals (from 85 p c alcohol)

(B) Acetyl derivative C, H18AcNO chief product obtained by heating morphine (1 mol) with acetic anhydride (1 mol) at 100° When less acetic anhydride is used a compound (C₁₇H₁₈AcNO₂)(C₁₇H₁₈NO₃) is obtained (Wright) Amorphous --B'HCl amorphous, v sol water Readily converted into morphine by boiling water, and hence usually gives a blue colour

with FeCl. B'EtI amorphous

(γ)-Acetyl derivative C17H18AcNO3 companies the (3)-isomeride to the extent of 25 p c Anhydrous crystals (from ether) — *B'HCl crystallises with difficulty, v sol water — B'Etl 1½aq crystals (from 85 p c alcohol)

Dr. acetyl derivative C17H17Ac2NO. [169°] Formed by heating morphine with excess of Ac,O at 85° (Wright, Hesse, A 222, 205)
The product is treated with water and dilute
NH,Aq, and extracted with ether Colourless prisms (from ether), v sol cold alcohol, m sol Gives no colour with FeCl. Converted by boiling water first into the (a) acetyl deriva-

tive, and then into morphine -B'HCl crystals, extremely sol water - B'sH2PtCls - B'MeCl Formed by heating morphine methylo-chloride with Ac₂O at 85° (Hesse) Needles, v e sol water—B'MeI Heated with AgOAc it yields the crystalline di-acetyl derivative of a compound C₁₄H₁₀O₂ [143°] (Fischer, B 19, 792) -B'EtI aq Crystals (B a W)

Di-propionyl derivative C₁₇H₁₇(C₂H₂O)₂NO₃. Formed by heating mor phine with propionic anhydride at 85° (Hesse, A 222, 207) White amorphous powder, v e sol ether, alcohol, and chloroform, sl sol water FeCl₃ gives no colouration — *B'HCl — B'₂H₂PtCl₅

(a)-Butyryl derivative C1,H18(C4H7O)NO3 Formed by boiling morphine (1 pt) with butyric acid (2 pts) for 6 hours (Beckett a Wright, C J 28, 16) Crystals (from ether) Gives no colour with FeCl₃—B'HCl more soluble and less readily crystallisable than the hydrochloride of the (a) acetyl derivative -B'2H2PtCla -B'EtI amorphous

(B) Butyryl derivative

 $\mathbf{C}_{17}\dot{\mathbf{H}}_{18}(\mathbf{C}_4\mathbf{H}_7\dot{\mathbf{O}})\dot{\mathbf{N}}\mathbf{O}_3$ An amorphous base, accom panying the preceding isomeride Gives a blue

colour with FeCl,

Di butyryl derivative C₂₃H₃₁NO₅ ie C₁₇H₁₇(C₄H₇O)₂NO₅ Formed by heating morphine (1 pt) with butyric anhydride (2 pts) for 3 hours at 140° (B a W) Amorphous Re solved by boiling water or boiling dilute alcohol into butyric acid and butyryl morphine -B'HCl amorphous Gives no blue colour with FeCl₃—B'EtI amorphous By boiling mor phine with a mixture of acetic and butyric acids, Beckett and Wright obtained a product which formed a crystalline double salt with the formula $(C_{17}H_{18}AcNO_3)(C_{17}H_{18}(C_4H_7O)NO_3)H_2Cl_2$ 8aq, re solved into its components by boiling water

C₁ H₁₈BzNO BenzoylderivativeFormed by heating morphine with benzoic acid at 160° (B a W), and by boiling the di benzoyl derivative with dilute alcohol Amorphous -B'HCl crystalline, v sl sol water

coloured by FeCl,

Di benzoyl derivative C17H17Bz2NO, [188°-191° cor] Formed from morphine and Bz_2O at 130° (B a W) or BzCl at 105° (Wright a Rennie, C J 37, 609, Dott a Stockman, Ph[3] 18, 231, cf Broockmann a Polstorff, B 13, 96) Prisms, insol water, sol hot alcohol Gives no colour with FeCl, —B'HCl amor phous -B',H,PtCl, -B'EtI +aq crystals

Acetyl benzoyl derivative
H.,AcBzNO, Formed from the (a) acetyl C₁₇H₁₇AcBzNO₃ Formed from the derivative and Bz₂O at 130° (B a W) line -B'HCl amorphous, v sol water -B'2H2PtCl6 -B'EtI 2aq crystals (from alcohol).

Succinoxyl derivative (C₁₇H₁₈NO₃)CO C₂H₄ CO₂H Formed by heating morphine (1 pt) with succinic acid (2 pts) at 180° (Beckett a Wright, C J 28, 689) Separates from alcohol in crystals (containing 4aq),

insol water and ether — B',H,PtCl,

Methylo-vodide C,,H,,NO,MeIaq Formed
by warming morphine with MeI and alcohol
(How, C J 6, 125, A 88, 338) If NaOEt is also present the product is codeine (Grimaux,

A Ch [5] 27, 273, C R 92, 1140)

Methylo - chloride C17H10NO.MeCl 2aq.

Formed from the methylo-rodide and AgCl (Hesse, A 222, 207) Long needles Its aqueous solution is coloured blue by FeCl₃ Ac_2O form C_1 , H_1 , Ac_2NO_3 MeCl $-(C_1$, H_1 , NO_3 MeCl) $-(C_1$, H_1 , NO_3 MeCl) $-(C_1$, H_1 , NO_3 MeCl) $-(C_1$, H_2 , NO_3 MeCl) $-(C_1$, H_3 Ac₂O forms

Methylo-hydroxideC₁₇H₁₉NO₂MeOH5aq Formed from the sulphate and baryta (Broockmann a Polstorff, B 13, 96) Colourless needles Reduces Ag₂O

Ethylo-rodide C17H19NO,EtI aq Formed by heating morphine with EtI and alcohol at 100° (How) Needles (from water).

Methyl-morphine v Codeine

D1-methyl-morphine C17H17Me2NO, Methyl $[a]_{D} = -208 \, 6^{\circ} \, \text{in a}$ morphimethine [118°] 4 pc solution in 97 pc alcohol at 15° Formed by heating codeine methylo-iodide (1 mol.) with aqueous KOH (1 mol), adding benzene, and shaking with acetic acid. The acid liquid is saturated with NaCl, and the hydrochloride of di methyl morphine then crystallises out free base is obtained by adding NaOH and ex tracting with ether (Hess, A 222, 220) Prisms, m sol ether, v sol water and alcohol Conc H.SO, gives a bluish violet colour Conc HNO. forms a yellow solution

Salts - B'HCl 2aq S 92 at 18° -

B H,PtCl, aq

Methylo - hydroxide

*C₁₇H₁₇Me₂NO₂MeOH Formed from the iodide and moist Ag₂O (Knorr, B 22, 181) Thick syrup Split up at 160° into NMe, and the phenanthrene derivative C14H2EtO2 Ac2O at 160°-200° forms acetyl methyl dioxyphenan threne C₁₄H_s(OMe)(OAc), dimethylamine, and di methyl oxyethyl amine NMe CH₂ CH₂OH (Fischer a Von Gerichten, B 19, 794)

(a) Methylo rodide C, H, Me2NO3MeI aq Formed from di methyl morphine and MeI dissolved in alcohol (Hesse, A 222, 225) Prisms

v sol hot water

(β) Methylo - todide C₁₂H₁₂Me₂NO₃MeI Obtained by adding KOH to a solution of the (a) isomeride, allowing the oily pp to crystallise, and adding KI to the mother liquor (Hesse, A 222, 227) Crystals

(a)-Methylo chloride

C₁₇H₁₇Me₂NO₃MeCl \(\frac{1}{2}\) aq Obtained from the (a) methylo iodide by treatment with AgCl Ac2O it forms C17H18AcMe2NO32 aq crystallising v sol hot water and alcoholin needles (B'MeCl),PtCl, 8aq

(β) Methylo chloride C, H, Me, NO, MeCl Formed from the (B) methylo iodide and AgCl Forms a neutral sulphate and a platinochloride

Acetyl derivative C₁₇H₁₆AcMe₂NO, [66°] Formed from di methyl morphine and Ac₂O at 85° (Hesse, A 222, 223) V sol alcohol and ether, m sol water, insol KOHAq a blue colour with conc H SO, -B'HCl aq B',H,PtCl,4aq -B'HNO,3aq -B',H,SO,8aq

Ethyl-morphine C, H18EtNO Codethyline Formed by heating S 2½ at 100° morphine (1 mol) with NaOEt (1 mol), alcohol, and EtI (Grimaux, C R 92, 1140, 1228, A Ch. [5] 27, 278) Hard brilliant laminæ (containing aq), v sol alcohol and ether, m sol water Ppd from solutions of its salts by KOH and Hard brilliant laminæ (containing Na,CO₂, but not by NH₂Aq Gives a blue colour with H₂SO₄ containing FeCl₃ —*B'HCl groups of alender needles—(C₁,H_{1a}EtNO₂)MeI Hard

bulky crystals, converted by moist Ag.O into a tertiary base [132°]

Di-ethyl-morphine *C1,H1,Et2NO iodide of this base appears to be formed by heating morphine with NaOH (1 mol) and EtI (2 mols) It is crystalline, and is converted by successive treatment with Ag.O and MeI into C17H17Et2NO2MeI, which crystallises from alcohol, and is converted by Ag₂O into an hydroxide which is split up on distillation into NMeEtPr and a derivative of phenanthraquinone C1.4H, EtO2 (Gerichten a. Schrötter, B 15, 2182)

Ethylene di-morphine C₂H₄(C₁,H₁₈NO₂) Di-codethine Dicodethylene Prepared by boiling morphine with alcoholic soda and ethylene bromide (Grimaux, C. R. 93, 67, A. Ch. [5] 27, 281) White needles (from alcohol), insol ether, v sol alcohol Blackens when heated, and de composes above 200° With H₂SO₄ and FeCl₃ it gives a blue colouration - *B"H2Cl2 Hard prisms

Morphinyl-sulphuric acid

C₁₇H₁₈(OSO₂H)NO₂ 2aq Morphine sulphonic acid Formed by shaking morphine (20 g) with KOH (8g), water (25 cc), and K.S.O. (15g) (Stolmkoff, H 8, 242) Silvery needles (from water), not decomposed at 160° y sl sol cold water, alcohol, and ether Hot dilute HClAq hydrolyses it to morphine and H2SO4 Does not give a blue colour with FeCl, Hot conc H SO. gives a rose colour, changing to violet poisonous than morphine, producing tetanus

Nitroso-morphine C17H18(NO)NO3 aq Formed by passing nitrous acid gas into morphine sus pended in water (E L Mayer, B 4, 121)

dish yellow powder, turned black by FeCl,
Trimorphine (C₁,H₁,NO₃), Formed by heating
morphine (30 g) with H.SO₄ (30 c c) and water
(30 c c) at 100° (Wright, C J 26, 220) Formed also by heating morphine (1 pt) with dry oxalic and (3 pts) at 145° (Becketta Wright, C J 28, 698) Amorphous, sol ether Gives a purple colour with FeCl, —B"H₂Cl, Amorphous Converted by cone hydrochloric acid at 100° into C₁₀,H₁₁,Cl N₆O₁₆6HCl, a brittle gum

Tetramorphine (C₁,H₁₀NO₂), Formed, together with trimorphine, by heating morphine with dilute H₂SO, at 100°-140° (Wright, C J 26, 220) Amorphous On heating with HClAq it forms the salt $(C_1, H_1, NO_3)_s(HCl)_s$ (?) On adding HCl to an aqueous solution of tetra morphine a flocculent pp of $(C_1, H_1, NO_3, HCl)_s$ is got $-(C_1, H_1, NO_3, L^2, L^2, C_3, Sulphomorphids.$ Obtained by heating morphine with dilute H2SO.

at 160° (Arppe, A 55, 96, Matthiessen a Wright, Pr 17, 455, Wright, C J 26, 220)

Apomorphine O₁, H₁, NO₂ Formed by heating morphine or code ine with HClAq at 145° for 2 or 3 hours (Matthiessen a Wright, Pr 17, 455) Formed also by heating morphine with aqueous phosphoric acid till the temperature reaches 185° (Wright, C J 25, 652) It is also one of the products when morphine is heated with aqueous ZnCl₂ for 20 minutes at 125° (Mayer a. Wright, C J 26, 211) Amorphous mass, which turns green in moist air Sl sol water, especially if it contains CO₂, sol alcohol, ether, and chloroform Emetic, O2 g of the hydrochloride being sufficient to produce vomiting. A solution of apomorphine hydrochloride gives with caustic alkalıs a white pp, quickly becoming black, with Na.CO, a white pp, turning green, with HNO, a blood-red colour, with FeCi, an amethyst colour, with K2Cr2O, an orange pp, with KI an amorphous pp, quickly becoming green, and with platinic chloride a yellow pp, decomposing on warming It reduces AgNO₃ AcCl yields a mono acetyl derivative (Danckwortt, Ar Ph 228, 572) -B'HCl crystals, sl sol cold water

Polymeride of apomorphine C₁₃₆H₁₃₆N₃O₁₆ (?) Formed, together with apomorphine and several bases, which form the hydrochlorides C_{1:s}H_{1,4}ClN₁O_{.2}H₁Cl₂(?), C_sH_sN₁O_sH_sCl₄(?), and C_sH_sH₃,ClN₁O_sH_sCl₂(?) by heating morphine with aqueous ZnCl₂ It forms a hydrochloride Bviii HaCla insol alcohol (Mayer a Wright)

Diapotetramorphine C₁₃₆H₁₄₈N₈O₂₂ Formed. together with apomorphine, by heating morphine with aqueous phosphoric acid (Wright) phous, rapidly darkening in air Evaporation with conc hydrochloric acid converts it into C₁₈₆H₁₄₆Cl₂N₈O₂₀8HCl Evaporation with HIAq and phosphorus yields $C_{186}H_{146}I_2N_8O_{20}8HI$ (Wright) the corresponding

Pseudomorphine C₁,H₁,NO, 1½ aq or C₃₄H₃₆N₂O₃ 3aq (Hesse, A 235, 229) Dehydromorphine Oxydimorphine Oxymorphine Discovered by Pelletier (1832) in Levant opium Occurs in morphine hydrochloride made by Gregory's method (Hesse, A 141, 87)

Formation -1 By heating a solution of morphine hydrochloride with $AgNO_2$ at 60° (Schutzenberger, Bl [2] 4, 176) -2 Byoxidising morphine with KMnO, potassium nitrite, or K₃FeCy₆, or by exposing its ammoniacal solution to the air (Polstorff, B 13, 86, cf Pelletier, A 16, 49)

Properties - White, microcrystalline powder (from NH, Aq), insol water, alcohol, ether, and chloroform, sol KOHAq and NH₈Aq, v e sol alcoholic NH, Levorotatory (Hesse, A 176, 195). Decomposed by heat without melting It is not affected by reducing agents. It is tasteless

and not poisonous

Colour tests -1 When evaporated with dilute H₂SO₄ until fumes of H₂SO₄ appear it be comes bluish green, and, on adding water, rosered, if HNO, or dilute NaNO, be now added the colour changes to deep violet Under similar circumstances morphia gives a rose red colour. turned brownish red by water, and raspberry red by HNO₃ (Donath, J pr [2] 33, 560) —2 Re sembles morphia in its reaction with FeCl, with molybdic acid in H2SO4 (Fronde's reagent), with HNO, and with HIO, For the reaction with iodic acid HCl must be absent NH₄Cl inter feres with these tests -3 Conc H₂SO₄ forms an olive green colour -4 Conc HNO₃ gives an in tense orange red colour, changing to yellow-5 A mixture of equal parts of cane sugar and pseudomorphine is coloured by H₂SO₄ blue, changing to dark green (Hesse, A 234, 255)

—B'HCl aq Minute needles \hat{S} 1 [a]_b = -103° 13'. — B'HCl 2aq Salts —B'HClaq at 20° B'HCl4aq B'HCl 3aq - B'HCl 6aq -- B'₂H₂PtCl₆8aq - B'HI aq B'HCl8aq B'H.Cl8aq — B'.H.clv.gosq — D. M. aq — B'H.gSO,4aq small colourless needles, sl sol cold water (Polstorff) — B'H.gSO,6aq lamine S 2 37 at 20°.—B'.H.Cr.O,6aq orystalline pp S. 1 at 18° — B'.H.Cl.O,6aq S 05 at 20°—B'.H.Cl.O,8aq — Tartrate B'O.H.O.8aq B',H,C,O,8aq — Tartrate B'C,I needles — B'C,H,O,6aq. S 24 at 18°.

Acetyl derivative C17H18Ac2NO. [276°] Formed by heating pseudomorphine (1 pt) with Ac₂O (2 pts) at 120° (Hesse, A 222, 235, 234, Crystallises from ether in prisms (containing 4 aq) V e sol alcohol, m sol ether and chloroform When mixed with cane sugar and dissolved in conc H.SO, at gives a dark green colour If the H₂SO, contain Fe₂(SO₄), the colour is at first blue —B'₂H₂PtCl₄6aq

Methylo - vodide — C₁,H₁,NO₂MeI 2aq

Formed by the action of HI on the crystalline body (C₁₇H₁₇NO₃)₂Me(OH)MeI, which is prepared by oxidising morphine methylo iodide with alkaline K₃FeCy₆ (Polstorff, B 13, 93) Small prisms

Methylo-hydroxide

C₁,H₁₇NO₃Me(OH) 8 aq Prepared by the action of moist Ag₂O on the iodide or of baryta on the sulphate Crystalline, v sol water, insol alcohol

Methylo sulphate

Obtained by ppg a (C₁,H₁,NO₃)₂Me SO₄ 4aq solution of the oxylodide with Ag2SO4 Leaflets, v sol hot water

MORPHOTHEBAINE v THEBAINE

MORPHOTROPY This term is applied to the relations between the crystalline form and the composition of those bodies which are chemi cally similar, and which are derived from the same parent body, v this vol p 89

MORRHUIC ACID C,H,,NO, ve

CH CH C(OH) C C,H CO,H (?) Oxy propyl pyridine dihydride carboxylic acid in cod-liver oil in a combination with glycerin and phosphoric acid, from which it is readily set free by acids and alkalis Obtained by extract ing the oil with dilute (35 pc) alcohol containing 5 pc of HCl (Gautier a Mourgues, C R 107, 740) Square flattened prisms or large lanceolate plates, insol cold, sol hot, water, v sol alcohol, ether, and alkalıs solutions have a disagreeable aromatic odour (Gautier, Bl [3] 2, 233) Morrhuic acid decomposes carbonates A solution of the potassium salt gives pps with lead acetate and AgNO2, but not with cupric acetate The silver salt is readily reduced, even in the cold Morrhuic acid forms a crystalline platinochloride, an amorphous aurochloride, and a hydrochloride which is de composed by boiling water On distilling with lime it yields a basic oil which forms a crystalline methylo iodide Potassium morrhuate is oxidised by KMnO, to an acid which ppts cupric acetate, and appears to be a pyridine derivative

MORRHUINE C19H27N3 An alkaloid oc curring, together with aselline C₂₃H₂₂N₄, in codliver oil (Gautier a Mourgues, Bl [3] 2, 228, C R 107,626) Thick oil, smelling like syringa, v sl sol water, v sol alcohol and ether Lighter than water Ppts copper salts Strongly alkaline It forms a very deliquescent hydrochloride crystallising in groups of needles, a crystalline platinochloride and a yellow aurochloride Morrhume constitutes one third of the total bases in the oil, and is a diaphoretic

and diuretic

MORTARS v CEMENTS, in Dictionary of Ap-PLIED CHEMISTRY

MOSAIC GOLD An alloy of Cu and Zn in equal parts, v Copper, allows of, vol 11 p 254, also DICTIONARY OF APPLIED CHEMISTRY.

MUCEDIN v PROTEIDS.

MUCIC ACID C.H.O. te CO,H CH(OH) CH(ŎH) CH(OH) CH(OH) CO,H Mol w 210 [206°-216°] (K a T) S 33 at 14°, 17 at 100° Formed by the oxidation of milk sugar, galactose, melitose, dulcite, gum arabic, gum tragacanth, and plant mucus with dilute nitric acid (Scheele, Opuscul 2, 111, Laugier, A Ch 41, 79, Berzelius, A Ch 92, 141, 94, 5, 95, 31, Malaguti, A Ch [2] 60, 195, 63, 86, Liebig a Pelouze, A 19, 258, Liebig, A 9, 24, 26, 160, Hagen, P 71, 531, A 64, 347, Johnson, A 94, 225, Schwanert, A 116, 257, Tollens, A 249, 220)

Preparation -1 Milk sugar (1 pt) is heated with HNO₃ (2 pts of S G 14) and water (2 pts) until red fumes appear The flame is then re moved until the reaction has abated The liquid is then evaporated, a further quantity (4 pt) of HNO, being added during the evaporation product is washed with water and dried (Klink hardt, J pr [2] 25, 43) The yield is 35 pc, cf Guckelberger, A 74, 348 — 2 Coarsely powdered milk sugar (100 g) is heated with HNO₃ (1200 c c of S G 115) in a basin on a water bath until the volume is greatly reduced (to 150 or 200 cc) After cooling, water (200 cc) is added, and after some days the mucic acid is filtered off and washed with water (500 cc) The yield is good (40 g) When galactose is treated in the same way the yield is 77 pc (Kent a Tollens, A 227, 221)

Properties - Colourless tables, sl sol cold water, insol alcohol It does not reduce Fehling's solution

Reactions -1 When boiled with water it changes to the isomeric paramucic acid -2 When heated with water at 180° it yields pyromucic acid -3 On dry distillation it yields CO2, pyromucic acid and some diphenylene When cautiously heated at 280° it forms a small quantity of de hydro mucic acid $C_4H_2O(CO_2H)$, which condenses on the neck of the retort as small crystals -4 Boiling nitric acid oxidises it to oxalic and racemic acids -5 On oxidation with H SO, and MnO formic acid is given off --6 Potash fusion yields acetic and oxalic acids --7 HIAq and phosphorus at 140° forms some adapte acid (Crum Brown, A 125, 19), and diphenylene oxide (Heinzelmann, A 193, 186)—8 PCl, forms di chloro muconic chloride C_aH₂Cl₄O (Liès Bodart, A 100, 325, Bode a Wichelhaus, A 132, 95)—9 When allowed to ferment for 9 months it yields alcohol and acetic, butyric, and traces of lactic acids (Béchamp, Bl [3] 3, 770) -10 Ba.S at 205° forms thiophene (β)-carboxylic acid -11 Fum ing HClAq (or HBrAq) at 100°-150° forms de hydromucic acid

Salts -- (NH₄)₂A" flat four sided prisms (from water), sl sol cold, v sol hot, water Decomposed at 220°-240° into pyrrole, pyrrole carboxylic amide, NH3, and CO2-NH4HA" aq needles or thin prisms More soluble in water than the normal salt — Na,A" 4\frac{1}{3}aq ransparent triclinic crystals — Na,A" \frac{1}{2}aq white powder — NaHA" 3\frac{1}{3}aq prisms — K,A" \frac{1}{3}aq granules S 12 5 Insol alcohol — K,A" 2aq (Schmidt a Cobenzi, B 17, 601) — KHA" aq decomposes at 150°-180° into CO, and pyromucate — BaA" 1½aq (dried at 100°) — CaA" 1½aq — MgA" 2aq (at 100°).—PbA" aq white pp — Pb,C,H,O,: ob-

tained by ppg ammonium mucate with basic lead acetate —CuA"aq (dried at 100°) bluish-white pp —FeA" 2aq (dried at 100°) yellow powder —K(SbO)A" —Na(SbO)A"(dried at 100°) Obtained by dissolving Sb₂O₂ in NaHA" Amorphous (Klein, C R 97, 1437) —Ag₂A" (dried at 100°) white pp —Methylamine salt Decomposed by distillation into methyl pyrrole and methyl pyrrole carboxylic methylamide -Ethylamine salt Decomposed by distillation into ethyl pyrrole, ethyl pyrrole dicarboxy lic diethylamide, and ethyl pyrrole carboxylic ethylamide (Bell, B 10, 1866) - Diethylamine salt Decomposed by heat giving off NHEt, — Aniline salt (C, H N)2H2A" Insol boiling alcohol, sol boiling water (Kottnitz, J pr [2] 6, Decomposed on distillation into phenyl pyrrole, CO2, aniline, and H2O On heating with water it forms mucic anilide

Methyl cther Me2A" Laminæ or flattened six sided prisms (from water), v sol hot water, ▼ sl sol hot alcohol Decomposes at 165°

Mono-ethyl ether EtHA" Formed by boiling Et2A" with alcohol (Limpricht, A 165, Crystals (containing 3aq), sol water and l Melts below 100°—NH,EtA"

Dr ethyl ether Et,A" [158°] S (alcohol of SG 814) 64 at 15 5° Formed by heating mucic acid (1 pt) with H SO, (4 pts) till it turns black, leaving it to cool, and adding alcohol (4 pts) (Malaguti, A Ch [2] 63, 86) Crystals (from boiling alcohol) Limpricht was not able to obtain this ether by the action of alcohol and HCl on mucic acid Mucic ether is reduced by sodium amalgam to an acid which strongly reduces Fehling's solu tior, and which may be readily re-oxidised to mucic acid (E Fischer, B 23, 937)

Isoamyl ether (CH₁₁)HA" Needles Amide C₈H₈O₆(NH₂) Mucamide S G 188 Formed from the normal ether and ammonia (Malaguti, C R 22, 854) Formed also by the action of ammonia on tetra acetyl mucio amide (Ruhemann, B 20, 3366) Minute crys tals (from water), v sl sol boiling water, insol alcohol and ether Converted by water at 140° into ammonium mucate On dry distillation it yıelds pyrrole carboxylıc amıde, paracyanogen, and a little pyromucic acid

Anilide C₆H₈O₆(NHPh) Formed by heating the aniline salt at 120°, or the ether with excess of aniline (Kottnitz) Plates, insol water, alcohol, and dilute acids

o Tolurde C.H.O.(NHC,H.)2 the preceding (K) Plates Tetra-acetyl derivative Formed like

C.H.(OAc),(CO₂H)₂ [266° cor] Formed by boiling mucic acid with Ac₂O and ZnCl₂ (Maquenne, Bl [2] 48, 720) Efforescent needles (containing 2aq), all sol water, v sol alcohol

Ethyl ether of the tetra acetyl deri-vative C.H.(OAc).(CO.Et). [177°] S (95 pc alcohol) 4 at 17° Formed by heating mucic ether with AcCl at 100° (Werigo, A 129, 195) Needles, sl sol ether, v sol boiling alcohol, v sl sol boiling water

Dr-phenyl-hydraside C₄H₄(OH)₄(CO N₂H₂Ph)₂ [240°] Formed by heating mucic acid with phenyl hydrazine hydrochloride and NaOAc on the water-bath (Bulow, A 236, 196, Maquenne, Bl [2] 48, 722) Pale yellow plates (from phenyl-hydrazine), v sl sol. water, alcohol, and ether Crystallises

unaltered from alcoholic potash
Paramucic acid S 136 in the cold, 58 at 100° Formed by evaporating an aqueous solu tion of mucic acid to dryness, dissolving the residue in alcohol, and allowing the alcoholic solution to evaporate in the air (Malaguti, A 15, 179) Crystalline, more soluble in water than mucic acid On recrystallisation from hot water it changes into mucic acid Paramucates, with the exception of the normal ammonium salt, are more soluble than the corresponding mucates, but their boiling solutions deposit mucates

Dehydromucic acid C,H,O,

Formation -1 By heating mucic acid in sealed tubes with HBrAq (saturated at 0°) at 100° for two days The product may be crystallised from water and separated from unaltered muoic acid by crystallisation of the Ba salt (Heinzelmann, A 193, 184) -2 By heating mucic acid with fuming HClAq at 145° (Seelig, B 12, 1083) —3 In small quantity by heating mucic acid at 180° (Klinkhardt) —4 By heating hydrogen potassium saccharate with conc HClAq at 150° (Sohst a Tollens, A 245, 19)

Preparation - Mucic acid (1 pt), conc HCl (1 pt), and conc HBr (1 pt) are heated 8 hours at 150° in sealed tubes The solid contents of the tubes are collected and distilled with steam If this steam be condensed it is found to contain dı-phenylene oxıde The residue is neutralised by ammonia, filtered, and mixed with HCl The dehydro mucic acid is then ppd Yield 20 p c

(Klinkhardt, J pr 133, 44)
Properties —Plates (from alcohol) or needles (from hot water) Does not melt at 320° sl sol cold water, alcohol, and ether May be sublimed

Reactions -1 FeCl, produces, especially on warming, in a solution of dehydro-mucic acid, a transparent gelatinous pp This result is pre vented by the presence of other acids -2 Bromine water converts it into fumaric acid, the reaction being $C_4H_2O(CO_2H)_2 + 8Br_2 + 3H_2O = C_2H_2(CO_2H)_2 + 2CO_2 + 6HBr - 3$ A mixture of HNO, and H2SO, converts it into nitropyromucie acid (q v) -4 Sodium amalgam reduces it to two acids of the formula CaHaOs, melting at 146° and 173° (Graebe a Bungener, B 12, 1079) The (a) acid [146°] crystallises in thin plates and forms the crystalline salts CaA" 3 aq, BaA" 4 aq, and Ag,A" aq (6)- acid [173°] forms large crystals (containing aq) and the salts CaA"1\u00e4a (amorphous), BaA"1\u00e4aq (needles) and Ag₂A" -5 On ary distillation it splits up into CO2 and pyromucie \mathbf{ac} id $(q \ v)$

Salts —BaA" 21aq —BaA" 6aq Sol water -CaA" 8aq —Ag₂A" white pp, decomposed by boiling water

Ethylether Et,A" [47°]

Chloride C.H.O(COCI). [80°] (c 245°) From PCl, on the acid (Klinkhardt, J pr 133, 46) Smells like POCl, Sol ether, alcohol, and CHCl. At 100° it sublimes forming flat needles Boiling water reconverts it into dehydro-mucic acid

Amide C4H2O(CONH2)2 Formed by the action of NH, on an ethereal solution of the chloride. Slender needles (from water) Nearly

insol cold water, alcohol, and ether Does not melt below 240°

MUCILAGE The gum of plants from which it is obtained by steeping these in hot water, which on cooling forms a jelly When linseed mucilage is strained through linen, and the filtrate mixed with alcohol and HClAq, a pp is obtained which after washing with alcohol and ether has the composition C₈H₁₀O₅ (Schmidt, A 51, 50, Frank, J pr 95, 484, Nageli a Cramer, Pharm Cent 1855, 426, Kirchner a Tollens, A 175, 215) Brittle gum, resembling bassorin $(q \ v)$, sol cold water, insol alcohol Dextrogyrate Insoluble ın ammoniacal cupric oxide Boiling dilute H2SO4 partially converts it into glucose

Quince mucilage is coloured blue by iodine, and gives no mucic acid on oxidation with nitric acid Boiling dilute H₂SO, yields a mixture of cellulose, gum, and sugar The mucilage from salep (Orchis mascula), from Tamarindus in dwa, and from some other plants, is also turned blue by iodine (v STARCH) Quince mucilage yields furfuraldehyde on distillation with dilute H₂SO₄, indicating the presence of arabinose or xylose It contains neither glucose nor galactose, since neither saccharic nor mucic acid is formed

on oxidation

Salep mucilage yields no furfuraldehyde on distillation with dilute H.SO,, but on oxidation it yields saccharic (but not mucic) acid It con tains glucose and mannose, but no galactose or arabinose (Gans a Tollens, A 249, 245)

MUCIN v Profess, Appendix C MUCOBROMIC ACID C.H Br O, ve

CHO CBr CBr CO H Semi aldehyde of di brorro-maleic acid [121°] Formed by adding bromine to pyromucic acid covered with a little water without cooling The product is boiled and evaporated, the yield being 70 pc of the theoretical (Schmelz a Beilstein, A Suppl 3, 276, Jackson a Hill, B 11, 1671 Am 3, 41) Formed also from $(\beta\gamma)$ di bromo pyromucic acid and hot dilute HNO3 (Hill a Sanger, A 232, 89) and by oxidation of di bromo maleic aldehyde

Properties - White plates, v sol alcohol, ether, and hot water, v sl sol cold water Red dens litmus and decomposes carbonates, but its

salts are very unstable

Reactions —1 When heated it partially sublimes, and the rest decomposes into HBr, di bromo maleic acid, and CO₂ (Hill, Am 3, 105) -2 Boiling baryta-water forms CO, bromo-ace tylene, malonic acid, and formic acid (Jackson a Hill, B 11, 289) Cold baryta water forms HBr and bromo maleic acid A cold paste of baryta and water forms bromo propiolic acid and β di bromo acrylic acid Baryta water at 0° forms mucoxybromic acid (q v) -3 Bromine water forms di bromo maleic acid (Hill, B 13, By heating with water and bromine (3 mols) in sealed tubes at 125° it is converted into penta and hexa bromo ethane, di bromo maleio acid, and tetra bromo butyric acid (Limpricht, A 165, 293) Bromine (1 at) at 145° forms dibromo maleic acid, mucobromyl bromide, and a little dibromo succinic acid —4 PBr, forms the bromide (v. infra) —5 Phenol (25 g.) dissolved in water (30 g.) containing KOH (17 5 g.) converts mucobromic acid (20 g) into 'phenoxy. mucobromic' acid C₁₀H₁BrO₄, which crystallises from water in prisms [105°] Phenoxy muco bromic acid forms the crystalline salts KA' and BaA', 3aq, and is converted by Ag₂O in hot water anto phenoxy-bromo-maleic acid C₁₀H,BrO₃, which crystallines in slender needles [104°], and forms a crystalline silver salt Ag₂A" (Hill a Stevens, Am 6, 188)—6 Moist Ag₂O oxidises it to di-bromo maleic acid Nitric acid acts in like manner—7 Alcoholic potassium nitrits forms a pp of K,C₃HN₃O₃, v sol cold water, converted by hot water into CO₂ HCy, HNO₂, and KC₃H,NO₄ Bromine in CS₂ converts the salt K₂O₃HN₃O₃, into C₃HBr₃N₂O₃ (Hill a Sanger, B 15, 1906)—8 KNO₂ at 50° forms the acid C₃H₃NO₄, which forms the crystalline salts NaA' aq, KA' aq, CaA'₂4aq, BaA'₂5aq, PbA'₂4aq, CuA'₂, and AgA'

Salts—BaA', white plates, sol cold water and alcohol—AgA' felted needles, insol water Ethyl ether EtA' [51°] (255°-260°) Formed from the acid, alcohol, and H₂SO₄ Large monoclinic crystals with aromatic odour KNO₂ converts it into crystalline C₆H₄KNO₇

Mucobromic acetic anhydride C.HBr.O. OAc [54°] Formed by heating mucobromic acid with AcCl at 120° Long needles, v e sol alcohol, ether, and chloroform

Bromide C₄HBr₃O₂ [56°] Obtained by heating mucobromic acid (1 pt) with PBr₃ (4 pts) at 115° Small slender prisms (from alcohol), sol alcohol, ether, benzene, chloroform, and CS₂ Boiling water slowly reconverts it into mucobromic soid

MUCOCHLORIC ACID C,H,Cl,O, t.e CHO CCI CCIO CHO CCI CCO2H or CHO CCI,C CO2H Semm. aldehyde of dr-chloro maletc acid [125°] Formed by passing chlorine into a solution of pyromucic acid (1 pt) in water (10 pts) at 0° in presence of iodine, the yield being 40 pc of the theoretical (Belstein a Schmelz, A Suppl 3, 276, Bennett a Hill, B 12, 655) Plates, v sol hot water, alcohol, and ether, insol ligroin and CS Split up by alkalis, even in the cold, into di chloro acrylic acid and formic acid

MUCONIC ACID (of Limpricht) $C_eH_eO_4$ is $CO_2H CH_2 C < CH CH_2 C < [100^\circ-125^\circ]$ Formed

by adding silver oxide to a hot solution of dibromo adipic acid [175°-190°] (formed by adding bromine to a warm solution of hydromiconic acid in HOAc), and decomposing the resulting silver salt with HCl or H₂S (Limpricht, A 165, 274) Large crystals, v sol water, alcohol, and ether Boiling baryta water decomposes it into CO₂ acetic acid, succinic acid, and another acid

Salts—BaA', 4aq nodules, v sol water
Muconic acid CO H CH CH CH CO H
[above 260°] S 02 at 15° Formed by the
action of alcoholic potash on βγ-di bromo-adipic
acid (Rupe, A 256, 22, Ruhemann a Blackman,
C J 57, 373) Branching white needles, al sol,
hot water, m sol hot alcohol and HOAc Completely decomposed by KMnO₄ in presence of
Na₂CO₅ Combines with bromine forming the
acid CO₅H CHBr CHBr CHBr CHBr CO₅H [c
250°] Sodium amalgam reduces it to hydromuconic acid [195°]

muconic soid [195°]
Salts — K.A" transparent plates, v sol
water, insol alcohol.—BaA"—PbA"—Ag.A"
curdy white pp The cupric salt is a bluish
green heavy amorphous pp

Methyl ether Me_2A'' [154°] Fan shaped groups of needles

Ethyl ether Et,A" [64°] Plates (from dilute alcohol)

Di chloro-mucomic acid C₆H₁Cl₂O₄ * & CO₂H.OH CCl CCl CH CO₂H S 10 at 100° Obtained by heating mucic acid or saccharic acid with PCl₂ and decomposing the resulting chloride with water (Liès Bodart, A 100, 325, Bode, A 132, 95, Bell, B 12, 1272, Limpricht, A 165, 253, Rupe, A 256, 6) Long needles (containing 2aq); v sl sol cold water, v sol alcohol, m sol. ether Not decomposed by boiling aqueous alkalis

Reactions—1 Reduced by sodrum amalgam to two acids of the formula $C_c H_0 O_1$, one of which melts at 195°, and yields malonic acid on oxidation, the other melts at 169°, and yields succinic acid on oxidation Boiling with sodium amalgam reduces it to adipic acid [148°]—2 Alcoholic potash at 190°-200° forms oxalic and acetic acids

Salts—The Ba and Ca salts are m solvater—Ag.A" unsoluble pp

water —Ag,A" insoluble pp

Methylether Me,A" [156°] Pearly plates,
v sol ether, hot alcohol, and HOAc

Ethyl ether Et A' [96°] From the chloride and alcohol (Wichelhaus, A 135, 251, Bell, B 12, 1273) Prisms

Chloride C₈H₂Cl₄O₂. Formed by the action of PCl₅ (6 mols) on muoic acid (1 mol) Large crystals (from CS₂), decomposed by moist air

A\$\text{#}\footnote{A}\text{Piydromuconic acid \$C_{\text{H}_2}O_2\text{H}\$ [195°] \$ 58 at 15° Formed by reducing di-chloro muconic acid with sodium amalgam or with zine dust and acetic acid White needles or prisms Converted by boiling NaOHAq into the isomeric acid [169°] Oxidised by KMnO, to oxalic and acetic acids Its Ba and Ca salts are less soluble in hot than in cold water Bromine added to its aqueous solution forms bromohydromuconic acid \$C_2\text{H}\$ CHC CHC CQ_2\text{H}\$ [183°], which yields an ether melting at 80° Bromine without water forms unstable dibromoadipic acid of the formula \$CO_2\text{H}\$ CHC. CHBr CHG CH

formula CO₂H CH₂ CHBr CHBr CH₂ CO H Ethyl ether Et₂A" (163° at 35 mm) Oul

 $A \, mide \, C_e H_e O_2 (NH.)_2$ [210°] (Ruhemann a. Blackman, $C \, J \, 57, \, 371$)

Δ^{aS} Hydromuconic and C_eH_sO₄ is CO₂H CH CH.CH₂ CH₂ CO₂H [169°] S 11 9 Formed by boiling the isomeric acid with aqueous NaOH (Rupe, A 256, 13) Nodular aggregates of plates, v sol hot, insol cold water, v sl sol ether Yields oxalic and succinic acids on oxidation with KMnO₄. Bromine forms a monobromo-derivative [160°] crystallising in branching needles, but no di bromo adipic acid

Methyl ether Oil Forms with bromine CO.Me CH, CH, CHBr CHBr CO.Me [85°]
MUCOXYBROMIC ACID C,H,BrO. 16

MUCOXYEROMIC ACID C₁₄, BrO₄ is CO₂H C(OH) CBr CHO [112°] Formed by the action of baryta water at 0° upon mucobromic acid (Hill a Palmer, Am 9, 148) Thick prisms, with beveiled ends, v sol water, alcohol, and ether, v sl sol chloroform, benzene, ligroin, and CS₂ FeCl₂ gives an intense garnet red colour. AgNO₂ forms a white crystalline pp On heating with baryta-water it yields oxalate and formate Bromine water converts it into bromalhydrate

CBr, CH(OH), and oxalic acid. Aniline yields

C,H,BrO,(NPh)

Salts - K2A" aq plates, v sol cold water, decomposed on warming—BaA" 2aq needles, al sol cold water, decomposed on boiling—PbA" yellow pp—Ag₂A" crystalline pp, ex plodes on heating or on moistening with HNO, Methyl ether Me₂A" Sticky liquid

Mono-ethyl ether EtHA" [89°] Prisms,

sol alcohol and ether

Dr-ethyl ether Et,A" Viscous liquid

'Anilmucoxybromic' acid

CO2H C(OH) CBr CH NPh [132°] Formed by the action of aniline hydrochloride on a dilute solution of mucoxybromic acid (Hill a Palmer, Pale yellow needles (containing Am 9, 156) aq), sl sol cold water, v sol alcohol, and ether FeCl, gives a brown pp Hot acids and alkalis set hydrazine salt (C₀H₄N) C₁₀H₄BrNO₃ aq
Salts -K₂A'' -BaA'₂ laq bright yellow crystalline pp -Ag A'' bright orange yellow pp

MUCOXYCHLORIC ACID C₄H₃ClO₄ ve CO₂H C(OH) CCl CHO [115°] Formed from mucochloric acid by treatment with a very slight excess of baryta, added slowly at a low tempera ture (Hill a Palmer, Am 9, 159) The yield is 73 pc of the theoretical Stout prisms, v sol water, alcohol, and ether, v sl sol chloroform and benzene With FeCl₂ it gives a deep garnet On heating with excess of baryta it yields oxalate and formate Bromine water forms oxalic acid and CClBr, CHO hydrazine yields an unstable condensation pro

duct Amine produces anilmucoxychlone acid Salts — K₂A" small tables — BaA" 2aq crystalline pp, sl sol cold water, v sl sol

dilute alcohol -BaA"aq -Ag A"

Mono-ethylether EtHA" [95°] Prisms, which may be sublimed, sol water, alcohol, and

ether, v sol boiling benzene

Dr ethyl ether Et,A" Viscous liquid Anilmucoxychloric acid C₁₀H₈ClNO₃ 1 e [147°] CO.H C(OH) CCl CH NPh Formed from mucoxychloric acid and aniline Pale yellow needles (containing aq), becoming bril liant yellow when anhydrous, al sol cold water, v sol alcohol and ether When it is heated with acids or alkalis aniline is split off FeCl₂ gives a deep brown pp Salts — K₂A'' — BaH₂A''₂ laq bright yellow

needles -Ag2A" bright crange pp -Phenylhydrazine salt PhN₂H₃H₂A" aq white crys talline mass, sl sol cold water, v sol alcohol

MUCUS OF PLANTS v MUCILAGE
MUNJEET The root of Rubia munjista, used in India as a dye stuff If ground munjeet is boiled with a solution of aluminic sulphate, and the red liquid filtered and acidified with HCl, a yellow pp is formed If the pp be boiled with alcohol, pectic acid remains undissolved, and the alcohol contains purpurin and munjistin They are separated by boiling dilute acetic acid, which dissolves munjistin

Munjistin is identical with purpuroxanthic acid, $C_{14}H_7(C\Theta_2H)O_4$ [231°] v DI OXY ANTHRA QUINONE CARBOXYLIC ACID (E Schunck & H Roemer, C J 33, 422, cf Stenhouse, Pr 12,

683 , 13, 86, 145 MUNTZ'S METAL An alloy of Cu and Zn, v. DICTIONARY OF APPLIED CHEMISTRY

MUREXIDE The ammonium hydrogen salt of Purpuric Acid (q v)

Formed by converting caffeine into di methyl alloxan (Fischer, B 14, 1912), and reducing this by H2S to tetra methyl alloxantin, which is then subjected to the action of air and ammonia (Brunn, B 21, 514, cf Rochleder, J pr 51, 405) Red prisms, sl sol water and alcohol Its aqueous solution is purple, resembling that of KMnO₄ Sublimes at about 230° Decolourised by potash (difference from murexide) Dilute HCl decomposes it, forming di methyl parabanic acid
MURIATIC ACID Synonymous with Chlor-

HYDRIC ACID, q v vol 11 p 5

MURRAYIN C₁₈H₂₂O₁₀ [170°] A glucoside obtained from the flowers of Murraya erotica by extracting with water (Blas, Z 1869, 316, De Vrij, Z 1876, 850, Hoffmann, Ar Ph [3] 14, 139) White powder, composed of small needles, si sol cold water, v sol boiling water and alcohol, insol ether Tastes bitter, but is not poisonous. Its solutions in alkalis and in Na₂CO₃ exhibit a greenish blue fluorescence and turn brown on heating The aqueous solution is not ppd by salts of Cu or Hg FeCl, colours its solution blue Lead subacetate gives a pp It reduces ammoniacal AgNO, and Fehling s solution on warming Dilute acids split it up into glucose and murrayetin

[c 110°] Murrayetin $C_{12}H_{12}O_5$ [c 110°] by boiling murrayin with dilute H SO₄ Formed (containing 3aq), sl sol cold, m sol boiling water, v sol alcohol, m sol ether Tasteless Its solutions exhibit strong greenish blue fluor escence, which is increased by KOH and by Na2CO3 FeCl3 gives a bluish green colour Lead

acetate gives, after a time, a yellow pp

MUSCARINE CH.NO 1 e CH(OH), CH, NMe, OH An alkaloid occurring, together with neurine, in the fly again (Agaricus muscarius) (Schmiedeberg a Koppe, J 1870, 875, Ruckert, N Rep Pharm 21, 193), in the fungus Amnarta Pantherina (Giacosa, J 1883, 1488), and in putrefying flesh (Gautier, Bl 2]
48, 13, cf Brieger, B 17, 2741) Formed by
oxidising neurine CH OH CH, NMe, OH with conc HNO, (Schmiedeberg a Harnack, C. C. 1876, 554) Deliquescent tasteless crystals, v e. sol water and alcohol, insol ether Its solution is strongly alkaline, ppts ferric and cupric hydrates from solutions of their salts, and acts as a narcotic poison antagonistic to atropine affected by boiling dilute acids or alkalis Gives amorphous pps with mercury potassium iodide and bismuth-potassium iodide

Salts -(CH(OH)2CH2 NMe2Cl)2PtCl2aq -

CH(OH)2.CH2 NMe, AuCl

Drethyl ether (HO)Me, N CH2 CH(OEt)2 Formed by heating chloro-acetal CH₂Cl CH(OEt)₂ (from di-chloro-ether) with tri-methyl amine (Berlinerblau, B 17, 1139) By heating the compound C₂H₂NBr CH₂CH(OEt)₂, formed by the action of bromo-acetal upon pyridine, with moist Ag₂O at 80° there is formed syrupy C₅H₃N(OH) CH₂ CH(OEt)₂, which is inappro MUSCLE 445

ethyl muscarine pyridine

MUSCLE Muscular tissue consists of fibres bound together into fasciculi by connective The fibres may be transversely structed (voluntary and cardiac muscle) or not (other in voluntary muscle) The plain or unstriated fibres are elongated cells with oval nuclei, and inclosed by a delicate envelope, they are singly The cardiac fibres have no sheath The voluntary muscular fibres have a well marked sheath or sarcolemma, under which are situated numerous nuclei, the contents of the sarcolemma (muscle plasma) have a semi liquid consistency during life Kuhne, and later Eberth, observed a nematode worm (Myoryctes Weis mann) crawling up the interior of a muscular fibre (Zet f wiss Zool 12,530), the contents of the sarcolemma are not, however, homogeneous, this is denoted by the transverse striping, which is probably an optical effect produced by the presence of certain more solid structures which are described as rods, membranes, tubules, and networks of fibres by different observers, these solid bodies are isotropous and are suspended in an anistropous (doubly refracting) viscous fluid (For the various theories of the histological structure of striated muscle during rest and on contraction, v Quain, Anat 9th edit, London, 1882, p 118 et seq, also O Nasse, Zur Anat u Physiol d quergestreiften Muskelsubstanz, Leip zig, 1882, Schafer, Pr 1891)

The sarcolemma is homogeneous and elastic. it is composed of an elastin like substance

(Ewald, Zert Brol 26, 1)

The muscle plasma, fluid during life, coagu lates after death, producing the stiffening called rigor mortis As blood plasma separates into a solid substance, fibrin, and a liquid residue, serum, after it is shed, so the muscle plasma separates into a clot composed of myosin and a liquid residue muscle serum Like the coagula tion of the blood this can be hindered by cold. and by squeezing the frozen muscles of the frog Kuhne obtained a liquid muscle plasma, which set into a clot which expressed serum subsequently when it contracted This occurred most readily at about 30°-40°C This can also be demonstrated in the muscles of warm blooded animals, but as rigor occurs there more rapidly, great expedition in manipulation is required Rigor mortis is also accompanied by the forma tion of sarcolactic acid

Admixture of muscle plasma with solutions of neutral salts prevents the coagulation of the Dilution of such salted muscle plasma brings about coagulation, this occurs most readily at 37°-40° C Saline extracts of rigid muscle differ from salted muscle plasma in being acid, but resemble it very closely in the way in which myosin can be made to separate from it, myosin in fact undergoes a recoagula-This is not a simple precipitation, it is first a jellying through the liquid, the clot subsequently contracts, squeezing out a colourless fluid or salted muscle serum This does not take place at 0°C, it occurs most readily at the temperature of the body, and is hastened by the addition of a ferment prepared from muscle in the same way as Schmidt's ferment is prepared from blood. The ferment is not identical with

printely termed by Lochert (Bi [3] 3, 859) di fibrin ferment, as it does not hasten the coagulation of salted blood plasma, nor does the fibrin ferment hasten the coagulation of muscle The recoagulation of myosin is also accompanied by the formation of lactic acid

The proteids of muscle plasma are—

1 Paramyosinogen, which is coagulated by heat at 47°C

2 Myosinogen, which is coagulated at 56°C. It is on the presence of this proteid that the power of fresh muscle juice to hasten the coagu lation of blood plasma depends

3 Myoglobulin, which differs chiefly from serum globulin in its coagulation temperature

(63°C)

4 Albumin, which is apparently identical with serum albumin a, coagulating at 73°C

5 Myo albumose, this has the properties of deutero albumose, and is identical with, or closely connected to, the myosin ferment

The first two proteids in the above list go to form the clot of myosin, paramyosinogen (called musculin by Hammarsten) is, however, not essential for coagulation, the three last remain in the muscle serum

Paramyosinogen, myosinogen, and myoglo bulin are proteids of the globulin class They are all completely precipitated by saturation with magnesium sulphate, or sodium chloride, or by dialysing out the salts from their solu tions They can be separated by fractional heat coagulation, or by fractional saturation with neutral salts

When muscle turns acid, as it does during rigor mortis the pepsin which it contains is enabled to act, and at a suitable temperature (35°-40°C) albumoses and peptones are formed by a process of self digestion. It is possible that the passing off of rigor mortis, which is apparently due to the reconversion of myosin into myosinogen, may be the first stage in the self digestion of muscle The usual theory with regard to the cause of the disappearance of rigor is that it is due to putrefaction setting in Cossar Ewart (Proc R Soc 1887) has shown that the disappearance of rigor and the appear ance of bacteria in the muscle are simultaneous. C Schipiloff's theory is that the lactic acid which is formed from the glycogen in muscle (Otto) produces rigor by precipitating the myosin, and the disappearance of rigor is due to more acid being formed, which redissolves the precipitate R Bohm has, however, shown that lactic acid is not derived from glycogen, but from a proteid source, and Latham has been able to deduce a formula which represents the formation of the acid from a combination of cyan hydrins such as he supposes a proteid

For the properties of myosin v PROTEIDS

For fuller details respecting muscle plasma and the proteïds of muscle consult Kuhne, Protoplasma, Leipzig, 1864, E Grubert, Maly's Jahrsber 13, p 307, J Klemptner, ibid p 310, E Kugler, *ibid* p 311, Demant, Zeit physiol Chem 3, 241, 4, 386, Halliburton, J Physiol 8, 133 Concerning the formation of acid during coagulation, v Kuhne, lc, Nasse, lc, Weyl a. Seitler, Zeit physiol Chem 557 (W & S suppose that the acidity is partially due to the formation of acid potassium phosphate, the phos446 MUSULE.

phonic anhydride being derived from the leathin and nuclein of the muscle), Berzelius (Lehrbuch, 9, 569), Du Bois Reymond (Gesammelte Abhandl sur allgem Muskel und Nervenphysik, Leipzig, 1877, 2, p 3), Heidenhain (Mechanische Leistung, p 143), R Böhm (Pf 23, 44), Hoppe Seyler (H 666), Latham (Brit Med Journal, vol 1 1886, p 630), C Schipiloff (Centralb f d med Wissens 1882, 291), Chittenden (Studies from Lab Physiol Chem Yale, 3, 116) Concerning the digestion of myosin, see Kühne and Chittenden (Zeit Biol 25, 358)

Pigments of muscle —Hæmoglobin is present in small quantities in nearly all muscles, it is contained in the muscle plasma, and it is especially abundant in the slowly contracting red muscles which occur in rodents, and occasionally also in other animals. In the gastropods, Limneus and Paludina, the muscles contain hæmoglobin, but there is none in the blood (Lankester, valso Hamoglobin)

Myohæmatin is one of a group of colouring matters called histohæmatins, i e pigments oc These substances are curring in the tissues probably respiratory in function, they have not been definitely separated from the tissues, but are probably proteid in nature and contain iron. myohæmatin can be recognised most easily, after soaking the muscle in glycerine, by the spectro scope, myohæmatın is contained in the muscle Myohæmatın exhibits four absorption plasma bands one just below D, two between D and E, and one just below F By soaking the muscle in ether, as a result of osmotic phenomena, the liquid separates out two layers, the lower of which is watery, yellowish-red in colour, and contains myohematin which presents a slightly different spectrum from that just described, viz one band between D and E and one between E In both cases the bands are very feeble and bwhen the pigment is oxygenated, but become well marked on the addition of reducing agents (MacMunn, Phil Trans 1, 1886, p 267, J Physiol 8, 51) Hoppe Seyler believes myohæmatin is altered hæmoglobin (Zeit physiol This, however, has been shown by Chem 13) MacMunn to be untenable (ibid)

Constituents of Muscle - Muscle contains on the average 75 pc of water, this percentage is higher in young animals and in cold-blooded animals, of the 25 pc of solids, 21 pc con sists of the proteids already described, and the remaining 4 pc of extractives and salts (cf Hofmann, Lehrbuch der Zoochemie, 104) The extractives are divided into (1) nitrogenous, viz creatine the most abundant (0 2 to 0 3 p c Voit, Z B 4, 77, increased by starvation, Demant, Zert physiol Chem 8, 387), creatinine, xanthne, hypoxanthine, and carnine, (2) non nitro genous viz fats, glycogen (C Bernard, C R 48, 678, Nasse, Pf 2, 97, Brucke, Sitz W 63, 214, Abeles, Med Jahrbücher, 1877, 551, Kulz, Z B 22,161), mosite (Scherer, Annal d Chem u Pharm 73, 322, Gauret a Villiers, C R 86, 486), sarcolactic acid and lactic acid In addition to the ferments already described (pepsin and myosın-ferment), muscle also contains an amylolytic ferment (Nasse, lc) Fresh muscle yields on ignition 1 to 15 pc of mineral matters, of which the most important constituents are potas-

sium and phosphoric acid (cf. Hofmann, l.c., and Bunge, Zeit physiol Chem 9, 60)

Contraction of muscle—The processes that occur in resting muscle are twofold one a change of matter, this chemical tonus, as it may be called, is lessened by curare poisoning, by which the influence of the nervous system over the muscular is shut off and the other set of changes is a change of the potential energy of chemical affinity into actual energy evidenced by the production of heat On the contraction of a muscle, there is a sudden acceleration of both these changes , viz an increase in chemical decomposition, and in the conversion of potential into actual energy which is evidenced as heat, electrical inequality, and mechanical motion. It is with the former of these, the chemical changes, that we have They may be briefly here specially to deal summarised as follows -

1 Change in reaction -The muscle ordi narily alkaline becomes acid, as it does during rigor mortis, and the acid produced is lactic acid The acidity can be easily demonstrated by litmus paper (Kuhne) It is the accumulation of this and other waste products, including alkaloidal substances (Mosso), in the muscle which produces fatigue -2 There is a relative increase of water (Ranke, Tetanus, cap 2, p 63) 3 The extractives soluble in water decrease, those soluble in alcohol increase (Helmholtz, Arch f Anat u Phys 1845 72, Ranke, lc 141, Heidenhain, Pf 3, 574)—4 Glycogen di minishes and sugar increases in amount (Ranke, Nasse, Pf 2, 97) -5 Creatine diminishes and creatinine increases in amount (Sarokin, Vir chow's Archiv, 28, Voit, Z B 4, 77)—6 Tetanised muscle is not able to oxidise pyro gallic acid as resting muscle is (Grutzner, Pf 7, 255) -7 Nitrates are converted into nitrites (Gschleidlen, ibid 8, 506) —8 Gaseous changes The amount of oxygen used and of carbonic acid given out increases, the amount of carbonic acid exhaled is never equal in amount to that of the oxygen absorbed, and during tetanus, i e continuous contractions, the quotient CO2 exhaled increases The following

O absorbed in the total numbers from Ludwig and Schmidt illustrate the differences in the gases of the blood leaving muscle during rest and activity

(For analyses of the gases of muscle v Hermann, Stoffwechsel der Muskeln, Ludwig, Sezel kow u A Schmidt, Sitz W 45, Sitzungsb der math phys Classe der k s Gesellsch der Wissensch 20, 12, Arbeiten aus d physiol Anstalt zu Leipzig, 1869 Full references of the literature on the effect of muscular exercise on respiration are given by Gamgee, Physiol Chem p 382).

No trustworthy results exist which show that the proteids of muscle undergo any change during activity, and the effect of muscular exercise on the nitrogenous excreta is very small, the increase of urea being quite out of proportion to the amount of work done (For experiments on dogs v. Voit, Untersuchungen über den Einfluss der Kochsalses des Kaffee's und der Muskelbewegungen auf den Stoffwechsel, München, 1860 For experiments on man, v Fick u Wis licenus, Veerteljahresschrift d nat Gesellsch in Zurich, 10, Parkes, Pr 15, 339, 16, 44, E Smith, Phil Trans 1862, 747, A Flint, Journ of Anat and Physiol 12, 91, F W Pavy, Lancet, 1876, North, Journ of Physiol 1, 171, Pr 39, 443)

Hermann's theory of muscular contraction .-No oxygen is obtainable from muscle in vacuo Hermann considers that the formation of carbonic acid is not simply the result of oxidation, but due to the splitting of a complex substance inogen into carbonic acid, lactic acid, and a gelatinous proteid myosin, the same occurs, but to a greater extent, in rigor mortis, the process of clotting especially going further Each contraction is thus the partial death of the muscle This is supported by the fact that the electrical conditions, like the chemical, are similar in dead and contracted muscle There is, however, no evidence to prove that a clot of myosin is formed Bernstein has more reat each contraction cently formulated a theory in which he seeks to show that changes in form, in composition, and in electrical potential are all parts of the same mechanism (Untersuch a d physiol Inst Halle, 1888) See also Burdon Sanderson (Re ports Brit Ass 1889) WDH

MUSTARD OILS The seeds of black mus tard (Sinapis nigra) contain potassium myronate, which, in presence of water, is decomposed by the ferment myrosin (also present in the seeds) into KHSO,, glucose, and allyl thiocarbimide or oil of mustard Small quantities of crotonitrile and free sulphur are formed in the hydrolysis (Forster, L V 1888, 209) Black mustard seed also contains a fixed oil which yields stearic and erucic acids on saponification (Darby, A 69, 1) The allyl thiocarbimide amounts to about 5 p c of the weight of the seeds White mustard seed (Sinapis alba) yields on pressure 36 pc of a fixed oil containing glyceiyl erucate The seeds also contain a glucoside, sinalbin $C_{30}H_{44}N_2S_2O_{16}$ which is decomposed by myrosin into sinapin sulphate $C_{16}H_{\gamma}NO_{2}H_{2}SO_{4}$, glucose, and an oil $C_{\gamma}H_{\gamma}NSO$ (Will, Z [2] 7, 89, A 199, 150) The term 'mustard oil' has been applied not only to the fixed and volatile oils from mustard seed, but also to all compounds of the form RN CS where R denotes a hydrocarbon radicle In this dictionary these compounds are described as thiocarbimides Thus the essential oil of black mustard is described as allyl thiocarbimide

MYCOMELIC ACID Č₄H₄N₄O₂½aq When alloxan is gently warmed with aqueous NH₃ it forms a yellow solution which deposits on cooling a transparent jelly of ammonium mycomelate, from the hot aqueous solution of which salt H,SO₄ ppts mycomelic acid (Liebig a Wöhler, A 26, 304) Mycomelic acid is also produced by boiling azulinic acid with water (Emmerling a Jacobsen, B 4, 951) and by heating uric acid with water at 180° (Wohler, A 103, 118, Hlasiwetz, A 103, 211) Gelatinous pp, drying up to a loose yellow powder Reddens litmus Almost insol cold water, m sol hot water and alkalis, insol alcohol and ether —AgC₄H₄N₄O₂.

MYCOSE v Trenalose and Sugars.
MYOCTONINE C, H., N, O, 5aq. [144°] Oc-

curs, together with lycaconitine, in Acontus lycoctonum (Dragendorff a Salomonovitch, C C 1886, 861) V sol chloroform and benzene, nearly insol ether (difference from lycacomitine) Poisonous, 01 g killing a frog Produces paralysis of the extremities of the motor nerves.

MYO-HEMATIIN v MUSCLE

MYOSIN v PROTEIDS and MUSCLE
MYRIGIN C₁₆H₂O₂. [72°] The portion of
bees'-wax insoluble in alcohol
mitate (Brodie, A 71, 144) Light feathery
crystals (from ether), readily saponified by alcoholic potash According to Nafzger (A 224,
251) myricin also contains an ether of oleic acid

MYRICYL ALCOHOL C₃₀H₃₂O te C₂₅H₃₅CH₂OH [85 5°] Obtained by saponifying carnauba wax, in which it occurs both free and combined (Maskelyne, C J 22, 87, Von Pieverling, A 183, 344, Sturcke, A 223, 294) According to Brodie (A 71, 147) myricyl alcohol is obtained by saponifying the myricin of bees'-wax, but Schwalb (A 235, 106) considers that the myricyl alcohol so obtained has the homologous formula C₃₁H₆₄O

Properties — Small white needles (from ether), almost insol cold alcohol, ether, and benzene, but readily soluble in these liquids when hot On heating with soda lime at 200° it forms

melissic acid C₂₂H₁₉ CO₂H [90°]

DI MYRICYL-AMINE C₂₂H₁₁, N to
NH(C₃₂H₄₁)₂, [78°] Formed by passing NH₄
for 24 hours over myricyl iodide at 120° (Von
Pieverling, A 183, 351) Crystalline, nearly
insol boiling alcohol and ether, v sol boiling
henzene

MYRICYL CHLORIDE $C_{3e}H_{el}$ Cl [64 5°] Formed from myrioyl alcohol and PCl_a (Von Pieverling, A 183, 348) Waxy mass (from ether), sol alcohol, benzene, and ligroin

MYRICYL CYANIDE C₂₀H₂₁CN [75°] Amorphous (Von Pieverling, A 183, 357) MYRICYL IODIDE C₂₀H₆₁I [70°] Formed

MYRICYL IODIDE C₃₀H₆₁I [70°] Formed by adding phosphorus and sodine in successive small portions to myricyl alcohol heated to 120° (Von Pieverling, A 183, 347) Plates (from ligroin), v sol hot alcohol and ether When heated with finely divided potassium it yields C₄₀H_{1/2} [102°] (Hell a Hagele, B 22, 502)

MYRICYL MERCAPTAN C₁₀H₁₁SH [94 5°] An amorphous yellow powder, formed by the action of alcoholic KSH on myricyl chloride (Yon Pieverling, A 183, 349) Sl sol boiling ether, ligroin, and alcohol

MYRISTIC ACID C₁₄H ,O₂ ve C₁₅H₂, CO₂H Mol w 228 [54°] (250 5° 1 V at 100 mm) Krafft, B 12, 1668, 15, 1724, 16, 1719) S G 24 8622 HF 107,000 (Von Rechenberg) H C 2,061,712 (Lougunne, A Ch [6] 11, 222) Oc curs as glyceryl ether (myristin) in nutmegative (from Myristica moschata) (Playfair, P M [3] 18, 202, A 37, 153, Fluckinger, N Rep Pharm 24, 213), in Otoba-wax or otobite (from Myristica totoba) (Uricosches, A 91, 369), in dika bread (prepared from the fruit of Mangifera Gabonensis) (Oudemans, J pr 81, 366) amounting to more than one half of the fatty acids contained therein, in the oil of Cyperus esculentus (Hell a Twerdomedoff, B 22, 1742), in small quantity in cocon unt oil (Gorgey, A. 66, 314), in common butter (Heintz, P 87, 267, 90, 137, 92, 429, 588, J pr 66, 1), in croton oil

(Schlippe, A 105, 1), and in Bicuhyba wax (from Myristica Bicuhyba) It occurs in combination with sethal in spermaceti (Heintz, A 92,291) It also occurs in the seeds of Nigella satua (Greenish, Ph [3] 11, 909, 1013) and in lycopodium spores (from Lycopodium clavatum) (Langer, Ar Ph [3] 27, 241, 289) Myristic acid is formed by fusing stearolic acid with potash (Marasse, B 2, 361)

Preparation -By saponifying nutmeg butter or myristin and distilling the acid obtained under

reduced pressure

Properties -Shining laminæ (from alcohol), insol water, v sol hot alcohol and ether A mixture of 30 pts myristic acid and 70 pts lauric acid melts at 35° Nitric acid (S G 1 5) readily oxidises it, forming various products (Uverdlinger, B 19, 1893) The dry distillation of the calcium salt yields myristone Distillation with MeOH in vacuo yields tridecane (Mai, B 22, 2133).

Salts -KA' crystalline soap, v sol water and alcohol, insol ether (Playfair) -NaA' BaA'2 minutelaminæ, v sl sol water and alcohol -MgA'₂Baq minute needles (Heintz) - CuA'₂ minute bluish green needles -PbA'₂ amorphous mass -(PbA'₂)₄Pb(OAc)₂ insoluble powder - AgA' amorphous powder

Ethyl ether Eth' [11°] (Lutz, B 19,1433) (295°) SG (liquid) 864 (Playfair) Formed from the acid, alcohol, and HCl Crystals, al.

sol alcohol and ether, m sol ligroin

Glyceryl ether C48H8,O8 or C
Myrstin Trimyristin [55°] and [49°] НĊ 6,601,895 (Louguinine) Occurs in the cases mentioned above, and also in large quantity in the fat of the oil nut (Myristica surinamensis) (Reimer a Will, B 18, 2011), and to the extent of 15 or 2 p c in cochineal (Liebermann, B 18, 1975) It is best obtained by extracting powdered nutmeg with ether (Masino, G 10, 72) Brilliant leaslets, v sol warm alcohol, ether, benzene, and CHCl, nearly insol cold alcohol It forms two varieties, melting at 55° and at 49°, which are interchangeable by heating 1° above the meltingpoint for half a minute (R a W, L)

Phenyl ether A'C₆H₅ [36°], (230° at 15

p-Tolyl sther A'C,H, [39°], (240° at 15 mm) (Krafft a Burger, B 17, 1379)
Chloride C₁₃H₂, COCl [-1°] (168° at 15

mm) Colourless liquid (Krafft a Burger)

Amide C18H27 CONH2 [102°] Formed by heating the glyceryl ether with alcoholic NH, at 100° (Masino, A 202, 173) or the ethyl ether with aqueous NH, at 250° Formed also by heating the ammonium salt at 230° in a sealed tube (Reimer a Will, B 18, 2016), and by the action of NH, on the chloride (Krafft a Stauffer, B 15, 1730) Plates (from alcohol), v sol benzene, alcohol, and chloroform, al sol ether, Insol. water Bromine and NaOHAq forms $C_{18}H_{27}$ NH CO NH CO $C_{19}H_{27}$ [103°]

Antités $C_{11}H_{27}$ CONHPh [84°] Prepared by boling the acid with aniline for some days

(Masino, G 10, 75) Silky needles, sol ether,

benzene, and chloroform

Natrile $C_{12}H_{27}$ CN [19°] (226 5° at 100 mm) S G $^{19}_{2}$ 8281, $^{99}_{2}$ 7724 Formed from the amide by distilling with $P_{2}O_{3}$ (Krafft a. Stauffer, B 15, 1730).

Myristic-benzoic-anhydride C18H2, CO O CO C6H3 [38°] Formed from BzC1 and potassium myristate (Chiozza a Malerba, A

91, 102) Silky laminæ, m sol ether Brome-myristic acid C₁₄H₂ BrO₂ Formed from myristic acid, amorphous P and Br (Hell a Twerdomedoff, B 22, 1745) Needles,

insol water, sol alcohol and ether

Tetra bromo-myristic aoid C14H24Br4O4 Formed from myristolic acid and Br (Masino) Amido-myristic acid $C_{14}H_{27}(NH_2)O_2$ [253°] Formed from bromo myristic acid and alcoholic NH₃ (H a T) Needles, insol alcohol

Phenyl-amido-myristic acid

C₁₄H₂₇(NHPh)O₂ [143°] Formed from bromo myristic acid and aniline (H a T) White mass, insol water, sl sol benzene, v sol alco hol Gives a dark green pp, with cupric acetate in hot alcoholic solution

Oxy-myristic acid C14H27(OH)O2 Formed by boiling bromo mylistic acid with excess of aqueous NaOH (H a T) Crystal line, insol hot water, v sol alcohol and benz ene – BaA'₂ flocculent pp, sl sol cold water, v sl sol hot water — AgA' white pp MYRISTIC ALDEHYDE C₁₃H CHO [53°]

(169° at 22 mm) Crystalline solid Prepared by dry distillation of a mixture of calcium myristate and formate (Krafft, B 13, 1415)

Isomeride —Tetradecoic aldehyde

MYRISTICIN C₁₂H₁₄O₃ 10 mm) S G ²⁵ 1 1501 [30°] (c 145° at Occurs in oil of mace (Semmler, B 23, 1803) Yields benzene when distilled with zinc dust Bromine forms

C₁₂H₁₄Br₂O₃ [105°] MYRISTICOL C₁₀H₁₈O (212°-218°) chief constituent of the volatile oil of nutmeg (Gladstone, C J 25, 11, Wright, C J 26, 549, 686) Resimified by heat P₂S₃ converts it into cymene PCl, yields a chloride, $C_{10}H_{15}Cl$ [100°], slowly split up on boiling into HCl and cymene MYRISTIN v Glyceryl ether of MYRISTIC

MYRISTOLIC ACID C, H2,O, [12°] Formed by passing chlorine into myristic acid heated to 100°, and decomposing the product with alcoholic potash (Masino, A 202, 175) Oil Not solidified by nitrous fumes Gives Petten kofer's reaction with sugar and H2SO4

MYRISTONE C 6H34CO SG = 801, $\frac{100}{4}$ = 792 Silvery plates Formed by distilling calcium or barium myristate with lime (Overbeck, P 86, 591, A 84, 290, Krafft, B 15, 1713) Does not combine with NaHSO, Oxim C28H34 C NOH [51°] Amorphous, sl sol alkalıs (Spiegler, B 17, 1575, M 5, 242) MYRISTONITRILE v Nitrile of Myristic

MYRONIC ACID C10 H19 NS2O19 (from μύρου a fragrant ointment) Occurs as potassium salt in the seeds of black mustard (Bassy, J Ph 16, 39, Ludwig a Lange, Z 1860, 430, 577, Will a Körner, A 125, 257), in horse radish (Winck ler, J 1849, 436), in rape seed (Brassica rapa), and in turnip seed (Brassica napus) (Ritthausen, J pr [2] 24, 273) This salt may be obtained by boiling mustard seeds (1 pt) with alcohol (6 pts), macerating the residue with cold water, and evaporating the aqueous extract after addition of a little BaCO. The free acid may be obtained by adding tartaric acid to a solution of the potassium salt, evaporating, and extracting with alcohol Syrup, readily decomposed by heat Its aqueous solution gives off H_2S on boiling An aqueous solution of myrosin splits it up into glucose, allyl thiocarbimide, and H,SO, Boiling baryta water forms a pp of BaSO, with evolution of allyl thiocarbimide Caustic potash solution acts vigorously, yielding allyl cyanide, NHs, glucose, and allyl thiocarb imide Conc HCl sets free H,SO,, boiling dilute H SO, yields H,S, glucose, H,SO,, and

NH₃ Zinc and HUIAq give on 122 Salts - KA' Groups of silky needles (from alcohol) or glassy prisms (from water), v è sol water, nearly insol alcohol, insol ether Tastes Its solution is hydrolysed by myrosin

 $KC_{10}H_{18}NS_{2}O_{10} = C_{6}H_{12}O_{6} + C_{3}H_{3}NCS + KHSO_{10}$ The hydrolysis is not brought about by emul sion, yeast, or saliva Water at 115° yields allyl cyanide, H2S, and sulphur Silver nitrate solution gives a pp C₄H₅NSAg₂SO₄ --BaA'₂ (at

100°) plates, v sol water
MYROSIN A proteid ferment contained in the seeds of black and white mustard and of many other cruciferous plants. It may be ob tained by exhausting white mustard with cold water, evaporating below 40° to a syrup, and ppg by alcohol (Bussy, J Ph 26, 44, Wincklei, Jahrb pr Pharm 3, 93) Its aqueous solution is coagulated by heat and by alcohol, when it loses its hydrolytic power, but it recovers this after a day's immersion in water It does not hydrolyse amygdalın

MYROXOCARPIN C. H.O. [115°] posited in crystals from an alcoholic solution of [182°] Minute cubes

white balsam of Peru (Stenhouse, A 77, 806) Trimetric crystals, a b c = 1 936 755 Insol water, v sol hot alcohol and ether Does not dissolve in acids or alkalis

A gum resin which exudes from Balsamodendron myrrha, a shrub growing in Arabia and Abyssinia The resin yields proto catechuic acid and pyrocatechin on potashfusion (Hlasiwetz a Barth, J 1866, 630) sides resin and gum (Buckner, N Rep Pharm 16, 76), myrrh contains a small quantity of an essential oil, boiling about 266°, SG 155 1 0189, $\mu_{\rm A}$ 1 5196 at 7 5°, $\mu_{\rm D}$ 1 5278, $\mu_{\rm H}$ 1 5472 (Glad stone, C J 17, 11) The oil quickly resimifies when exposed to atmospheric oxidation It contains $C_{22}H_{22}O$ (263°) (Fluckiger, B 9, 471) According to Kohler (Ar Ph 228, 291) myrrh contains a gum $C_1H_{10}O_3$, a resin $C_{2e}H_{41}O_2(OH)_{4}$, two dibasic acids $C_{12}H_{16}O_8$ and $C_{2e}H_{22}O_{9}$, and 7 p c of an essential oil $C_{10}H_{14}O$

MYRTLE OIL A volatile oil obtained from the berries and leaves of the myrtle (Myrtus communis) (Riegal, Pharm Centr 1850, 319) contains a terpene C₁₀H₁₆ (160°-170°), S G 188 891, μ₄ 1 462 at 18°, μ_p 1 468, μ_H 1 488 (Glad stone, J 1863, 548) Jahns (Ar Ph [3] 27, 174) found in Spanish oil of myrte pinene $C_{10}H_{16}$ (159°) [a]_D = 36 8, and cineol (170°)

MYTILOTOXINE C₆H₁₅NO₂ mussels (Mytilus edulis) and in putrid flesh (Brieger, Die Ptomaine, Gautier, $B\overline{l}$ [2] 48, 13) Its hydrochloride crystallises in tetrahedra, and 18 very poisonous, but gradually decomposes, losing its poisonous properties - B'HÂuCl.

N

MANDININE C₁₉H₁₉NO₄ Occurs in the root bark of Nandina domestica of Japan (Eijkman, R T C 3, 197) White amorphous powder, insol water, v sol alcohol, ether, benzene, and chloroform Poisonous Gives the alkaloidal re H2SO4 forms a reddish-violet colour, changed by a drop of HNO, to an intense blue Nitrio acid gives a green colour changing to brown—B',H,PtCl, turned blue by H,SO,

NAPHTHA v Petroleum (β)-NAPHTH-ACRIDINE C₂₁H₁₈N ι e

O₁₀H₆ [216°] Formed by the action

of methylal, and HCl upon (8) naphthyl amine (Reed, J pr [2] 34, 160, 35, 317) Long, straw-yellow, needles, v sol alcohol, v sl sol ether The alcoholic solution fluoresces dark blue

Netrate B'HNO, small needles
Pecrate B'C, H, (NO,), OH amorphous Derivative v PHENYL NAPHTHACRIDINE NAPHTHALDEHYDE v NAPHTHOIC ALDE-

NAPHTHALENE C₁₀H₈ Naphthalm Mol w 128 [80·2°] (Reussert, B 23, 2248), [80°] (Landolt, Z P O 4, 349), [79 5°] (Vohl), [79°] (Lossen a Zander, A 225, 111), [80 06°] (Mills, P M [5] 14, 27) (218°) at 760 mm (Vohl, J Vol III

pr 102, 29, Crafts, Bl [2] 39, 282), (217°) at 740 mm S G 15 1 152 (V), 4 1 145 (Schroder, B 12, 1613) S G (liquid) 12 978 (Kopp, A 95, 329), 79 982 (L a Z) H C v 1,232,400 H C p 1,233,600 (Stohmann),1,245,000 (Berthelot a Vieille, Bl [2] 47, 863), 1242000 (Berthelot, A Ch [6] 13, 302, 326) H F 17 600 (Stohmann Meley a Langhen A pr - 17,600 (Stohmann, Kleber, a Langbein, J pr [2] 40, 90), - 29,000 (Berthelot a Vieille, A Ch [6] 10, 442), -42,000 (von Rechenberg) S V 149 2 (L a Z), 148 (Lossen, A 254, 53), 145 46 (Ramsay), S V S 130 61 (Schiff) R_Q R_{op} 74 12 m a 6 66 p c alcoholic solution (Kanonni koff), 71 78 (Nasını a Bernheimer, G 14, 153 15, 93) S (toluene) 32 at 165°, S (alcohol) 5 29 at 15° (Biechi, B 12, 1978) Its absorp tion in the ultra violet spectrum has been studied by Hartley (C J 39, 161)

Occurrence -In petroleum from Rangoon (Warren a Storer, Mem Amer Acad 9, 208) In coal tar, from which it may be obtained by shaking the fraction 180°-220° with aqueous NaOH and then with dilute HaSO, and distilling the residue alone or with steam (Garden, Thom son's Annals, 15, 74, Faraday, Tr 1826, Kidd, B.J. 8, 186, Reichenbach, S 61, 175, 68, 233).

Formation.-1 A product of the passage through a red hot tube of the vapour of the following substances -petroleum, alcohol (Reichenbach, B J 12, 307), ether, acetic acid, essential oils, toluene (Ferko, B 20, 660), xylene, ψ -cumene, a mixture of ethylene with benzene, with styrene, with anthracene or with chrysene (Berthelot, Bl [2] 6, 272, 279), ethylene alone, acetylene, a mixture of benzene and acetylene (Berthelot, Bl [2] 7, 218, 278, 30b), oil of turpentine (Schulz, B 9, 548), wood-tar (Letney a Atherberg, B 11, 1210, 1222) -2 By passing over red hot quicklime the vapour of the bromide of phenyl butylene derived from benzyl bromide, allyl iodide and sodium (Aronheim, B 6, 67, A 171, 233) —3 By pass ing the vapour of isobutyl benzene over heated lead oxide (Wreden a Znatovitch, B 9, 1606) -4 By distilling colophony and gum benzoin with zinc dust (Ciamician, B 11, 269) -5 By heating dimethyl aniline (1 pt) with bromine (1 pt) at 115° (Brunner a Brandenburg, B 11, 697) 6 By oxidising pyrenic acid and distilling the resulting naphthalene tetra-carboxylic acid with slaked lime (Bamberger a Philip, B 19,1999) 7 By hydrolysis of its sulphonic acids takes place when superheated steam is passed through a solution of naphthalene (3) sulphonic acid in dilute H.SO, at 135° (Armstrong a Miller, C J 45, 148)

Synthesis—By dry distillation of the silver salt of tetra hydro naphthalene di carboxylic

acid C_eH₄CH₂CH₂CH₂CH₂Which acid is formed

by the action of o xylylene bromide C₀H₄ CH₂ Br on di-sodio ethane tetra carboxylic ether C₂Na₂(CO,Et)₂, and boiling the product with alco holic KOH Naphthalene is also formed by passing the tetra hydro naphthalene di carboxylic acid through a red hot tube (Baeyer a Perkin, B 17, 448) (v NAPHTHOL and NAPHTHALENE DEBIVATIVES, Constitution of)

Purification — Commercial naphthalene may be purified by sublimation. It may also be purified by repeatedly heating with a little H₂SO₄ (best with MnO₂) at 180° and distilling with steam (Stenhouse a Groves, B 9, 683)

Properties — Monoclinic tables, insol cold, almost insol hot, water, v sol alcohol, ether, fatty and essential oils, and HOAc Volatile with steam, 1 pt distilling over with about 570 pts of water (Naumann, B 4, 646, 10, 2014, 2100, 11, 33) Burns with smoky flame Boil ing naphthalene dissolves S, P, and the sulphides of As, Sb, and Sn, it also dissolves indigo, iodine. HgCl., HgL., and As.O.

iodine, HgCl₂, HgI₂, and As₂O₃

Reactions—1 Chlorine forms derivatives by substitution and by addition (Laurent, A Ch 49, 218, 52, 275, 69, 214)—2 Bromine forms derivatives by substitution—3 Nitric acid forms nitro and di nitro naphthalene—4 The vapour of aqua regia in the cold forms C₁eH₂Cl₄ and C₁eH₂Cl₅ (Bunge, B 4, 289)—5 Phosgene has no action (Berthelot, Bl [2] 13, 301)—6. The vapour passed through a red hot tube yields carbon, methane (Kletzinsky, J 1865, 561), and dinaphthyl (Ferko, B 20, 662) When passed through a red-hot tube together with hydrogen it is mainly unaltered, but yields some acetylene and benzene (Berthelot, Bl [2] 6, 281) When passed together with acetylene through a red-hot tube it yields much anthracene—At a white

heat it reacts with benzene forming anthracene (Berthelot) When passed through a red-hot tube containing charcoal it yields some di-naphthyl When passed with ethylene through a red-hot tube it yields acenaphthene, phen anthrene, and dinaphthyl (Ferko, B 20, $6\hat{6}$ 2) --7 Saturated HIAq at 280° yields the dihydride $C_{1o}H_{1o}$, and finally ethyl and diethyl benzene and decane (Berthelot, J 1867, 709) When heated with cone HIAq and red phosphorus the products are naphthalene hexahydride, and oily $C_{10}H_{18}$ (173°-180°) and $C_{10}H_{20}$ (158°-158°) (Wreden, A 187, 164) —8 Boiling aqueous KMnO, oxidises it to phthalic acid Aqueous K₂Cr₂O₇ and H₂SO₄ yield phthalic acid and dinaphthyl (Lossen, A 144, 71) Dilute HNO₃ at 130° also yields phthalic acid (Beilstein a Kur batow, A 202, 215) A mixture of CrO, and HOAc oxidises it to naphthoquinone Oxidation with MnO2 and H.SO4 yields dinaphthyl and a resinous acid C₂₀H₁₄O₄, which forms the amor phous salts Pb₂H''₂, PbHA''', and Ag,HA'' (Lossen) —9 KClO₃ and H SO₄ form phthalic acid, di chloro-naphthalenes, and syrupy chloro oxy naphthalic acid C₁₀H,ClO, (Hermann, A 151, 79)—10 CrO Cl₂ yields di chloro naphtho quinone -11 Aqueous hypochlorous acid forms C₁₀H₈(HOCl), crystallising in prisms, sl sol water, converted by alcoholic potash into C10H8(OH)4 which crystallises in prisms, almost insol water, v sol alcohol, and forms an in soluble lead compound Pb2C10H8O4 (dried at 100°) and a sulphonic acid which yields a crystalline calcium salt $CaC_{10}H_{10}S_2O_{10}$ (Neuhoff, A 136, 342) —12 When heated with excess of AlCl₃ it forms benzene and hydrides of naphthalene At 160° iso dinaphthyl is formed (Friedel a Crafts, Bl [2] 39, 195, C R 100, 692) -13Methyl chloride in presence of AlCl, forms C, H, [181°] crystallising in plates, v sol hot ether, sl sol cold alcohol (Bischoff, B 23, 1905, cf Liebermann, A 163, 122, Furth, B 16, 2171) -14 Iodine at 250° appears to form a compound $C_{40}H_{23}I$ (Bleunard a Vrau, C R 94, 534) -15On passing a mixture of cyanogen and naph thalene vapour through a red hot tube there is formed the nitrile of (a) naphthoic acid—16 Heating with chloride of sulphur yields di chloro naphthalene (Laurent, A 76, 298) -17 Nitric peroxide forms nitro and di nitro naphthalene and, at 100°, the compounds C₁₀H₈O₄ [225°] and C₁₀H₄O₄ [131°] (Leeds, Am Ch 2, 283) —18 When heated with potassium it forms a black powder C₁₀H₈K₂, which is decomposed by water, yielding KOH and C₁₀H₁₀ (Berthelot, Bl [2] 7, 110) —19 Naphthalene (2 pts) fused with anti monrous chloride (3 pts) yields on cooling deliquescent crystals of $(C_{10}H_8)_23SbCl_3$ (W Smith, Naphthalene taken inter-C J 41, 411) --20nally appears in the urine as (β) naphthol and (A) naphthoquinone (Edlefsen, C'C 1888, 1007)

Combinations with nitro compounds

-C₁₀H₄C₄H₄(NO₂)₂[1 8] [53°] Prisms (Hepp, A 215, 379) -C₁₀H₄C₄H₄(NO₂)₂ [1 4] [119°] White needles, v sl sol alcohol, separated into its components by distillation with steam — C₁₀H₄C₄H₄Cl(NO₂)₂ [1 2 4] [78°] Long white needles (from alcohol), decomposed by heating with potash or aniline, naphthalene being set free (Willgerodt, B 11, 608) -C₁₂H₄C₃H₄(NO₂)₂. [152°] White needles, deposited from a mixture

of the alcoholic solutions of naphthalene and tri nitro benzene (Hepp, A 215, 377) tri nitro benzene (Hepp, A 215, 877) —

C₁₀H₂C₄L₂Cl(NO₂)₂ [96°] Flat canary-yellow

needles (Liebermann a Palm, B 8, 378) —

C₁₀H₂C₄H₂Me(NO₂)₂ [61°] Formed by mixing

naphthalene and di-nitro-toluene dissolved in benzene (Hepp) — $C_{10}H_8C_6H_2Me(NO_2)_3$ Formed from (a) tri nitro toluene and naphthalene in alcoholic solution (Hepp) Needles — $C_{10}H_{*}C_{*}H_{2}Me(NO_{2})_{*}$ [100°] Formed from (\$\beta\$)-tri nitro toluene and naphthalene Yellowish Yellowish needles (from alcohol) — C₁₀H₈C₈H₂Me(NO₂)₃ [89°] Formed from (γ) tri-nitro-water.

C₁₀H₂C₄H₂(NO₂)₂NH₂ [169°] Orange
C₁₀H₄C₄H₄(NO₂)₂OH Yellow needles
Z 1868, 218) — C₁₀H₂C₅H₂(NO₂)₄OH Formed from (γ) tri-nitro-toluene (H) [169°] Orange prisms Yellow needles (Gruner, [78°] Formed from (8)-tri nitro phenol and naphthalene (Henriques, A 215, 332) \forall e sol alcohol — $C_{l_0}H_sC_sH_s(NO_s)OH$ [100°] Formed from naphthalene and (γ) tri nitro phenol (Hen riques) Golden needles (from alcohol), sì sol alcohol—C₁₀H₈C₆HMe(NO₂)₂OH [106°] From naphthalene and tri nitro o cresol (Nolting a Collin, B 17, 271) Yellowish needles (from acetone) -C₁₀H₈C₆HMe(NO₂)₃OH [127°] From naphthalene and tri nitro m-cresol (Nölting a Salis, B 15, 1862) $-C_{10}H_8C_4H_2(NO_2)_2S$ Yellow needles (from benzene) Formed from naphthalene and di nitro thiophene (Rosenberg, B 17, 1778)

Pieric acid compound

C₁₀H₈C₀H (NO₂₎₃OH [149°] Golden yellow monoclimic needles, sol alcohol, ether, and benzene Slowly separated into its components

by boiling water

Naph halene dichloride $C_{10}H_8Cl$ Formed by passing chlorine over naphthalene $KClO_3$ and HCl may also be used (E. Fischer, B. 11, 735, 1411). Oil, miscible with ether, in sol alcohol. Begins slowly to decompose at 40° – 50° into HCl and chloro naphthalene. Alcoholic potash also converts it into chloro naphthalene. Sodium or sodium amalgam at 150° converts it into naphthalene.

Naphthalene tetrachloride C10H,Cl Mol R_∞ 105 35 in a 2 39 pc [182°] chloroform solution (kanonnikoff) Formed by passing a rapid current of chlorine over naph thalene until the product, after having become liquid, thickens again, when it is washed with ether and crystallised from benzene Formed also by treating naphthalene with a saturated solution of chlorine in CHCl₂ (Grimaux, B 5, 222, Schwarzer, B 10, 379), by chlorinating naphthalene in direct sunlight (Leeds a Ever hart, A C J 2, 205), and by the action of KClO₄ and HCl on naphthalene (Fischer, B 11, Large monoclinic prisms, insol water, sl sol alcohol, m sol ether, v sol benzene and petroleum Sublimes at 225°-230° Decomposed on distillation into HCl and (a)- and (B) di chloro naphthalenes (Krafft a Becker, B 9, 1088) Alcoholic potash forms (a) and some (i) dichloro naphthalene reconverted into naphthalene on digesting with iron (Zinin, B 4, 288) Boiling dilute AgNO₃ slowly converts it into C₁₀H₄(ClO)₂ [196°] When boiled with water it yields C₁₀H₄Cl₂(OH)₂, which crystallises in prisms (from ether) [156°], S 3 3 at 100°, and is decomposed on divillation with VCl. decomposed on distillation with HCl into water, HCl, and chloro-naphthol Zn and H₂SO₄ re

duce it to (a) naphthol It gives rise to $C_{10}H_{5}Cl_{2}(OAc)_{2}$ [131°] and $C_{10}H_{5}Cl_{2}(OBz)_{2}$ [150°]

The existence of an isomeric northelene

The existence of an isomeric naphthalene tetra-chloride [118°] has been denied by Atterberg (B 11, 1223, of Fischer, B 11, 735)

Naphthalene tri chloro bromide C₁₀H_cCl₂Br. Formed from the tetrachloride and bromine; after 48 hours the product is washed with warm alcohol and crystallised from ether Prisms

Naphthalene dihydride C10H10 [15 5°] (212°) V D 47 (calc 456) Occurs coal tar oil (Berthelot, Bl [2] 9, 288) Occurs in heavy Formed by heating naphthalene with conc HIAq for a short time at 280° (Berthelot), and by reducing naphthalene dissolved in isoamyl alcohol with sodium (Bamberger a Lodter, B 20, 3073) Naphthalene dihydride is formed by distilling the bromide of naphthalene tetra hydride, or by heating it with alcoholic KOH (Graebe a. Guye, It is likewise obtained by the B 16, 3032) action of sodium on an alcoholic solution of the nitrile of naphthoic acid (Bamberger a Lodter, B 20, 1704) and, as a by product, when (β) naphthylamine dissolved in isoamyl alcohol is reduced with sodium (Bamberger a Muller, B 21, 859)

Properties—Tables Does not combine with pieric acid By treatment with bromine dissolved in chloroform it is converted into the dibromide C₁₀H₁₀Br₂, which crystallises in thick colourless prisms, v sol alcohol and ether, and gives off HBr on heating (B a. 1.)

gives off HBr on heating (B a L)

Naphthalene dihydride C₁₀H₁₀ (200°)

Formed by distilling the dihydride of naphthoic acid with soda lime (von Pechmann, B 16, 517)

Liquid

Naphthalene tetrahydride C, H, $C_{\sigma}H_{\bullet}{<_{\mathrm{CH}}^{\mathrm{CH}_{2}}}_{\mathrm{CH}_{2}}^{\mathrm{CH}_{2}}$ (205°) at 716 mm Formed by heating naphthalene with HIAq at 280° (Berthelot), with PH,I at 180° (Baeyer, A 155, 276), or by adding sodium to its solution in isoamyl alcohol (Bamberger a Kitschelt, B 23, 1561) Formed also by sus pending the tetrahydride of (a) naphthyl hydrazine (1 pt) in boiling water and allowing a solution of cupric sulphate (2 pts) to drop in slowly, nitrogen is evolved, and the naphthalene tetrahydride may be separated from ppd cuprous oxide by steam distillation (Bamberger a Bordt, B 22, 631) Prepared by heating naphthalene (10 pts) with HI (9 pts) and amorphous phos phorus (3 pts) for 8 hours at 220°-225°, the yield is good (8 pts) (Graebe a Guye, B 16,

3028, of Graebe, B 5, 678)

Properties—Oil, slowly turning brown in air Smells like naphthalene—Its solution in chloroform absorbs bromine, giving off HBr—It immediately decolourises an acid solution of KMnO4, and is oxidised to C4H4(CO2H) CH2 CH2 CO2H (Bamberger)—The compound obtained by Baeyer and by Graebe yielded phthalic acid on oxidation by KMnO4 and may perhaps not be identical with Bamberger's tetrahydride—When passed through a red hot tube it is resolved into naphthalene and hydrogen

Naphthalene hexahydride C₁₆H₁₄ Hexahydronaphthalene (200°) (G a G), (205° at 764 mm) (A) S G § 9419 C E (0°-26 3°) 000817 (Lossen a. Zander, A 225, 112) R₂₀ 71 15 (Nasını a Bernheimer, G 15, 93) S V.

171 2 (Lossen, A 254, 53) Formed by heating naphthalene with conc HIAq and phosphorus (Wieden a Znatovitch, B 9, 278, 1606, A 187, 164) Prepared by heating naphthalene (67 pts) with HI (100 pts) and amorphous phosphorus (30 pts) for 10 hours at 240°-250° (Graebe a Guye, B 16, 3031), or by heating naphthalene (10 g), amorphous phosphorus (3 g), and HIAq (9 g, boiling at 127°) at 235° for 7½ hours (Agrestini, G 12, 495) Liquid, which absorbs oxygen from the air Does not combine with picric acid Reacts with bromine, giving off HBr, and forming a product which is converted by alcoholic potash into C₁₀H₉Br (270°)

Naphthalene octohydride $C_{10}H_{16}$ (185°-190°) S G § 910, § 892 Formed by heating naphthalene (5g) with HIAq (9g of S G 17) and red phosphorus for 15 hours at 260° (Guye, Bn 2, 138) Liquid, smelling like oil of turpentine Absorbs oxygen from the air

References — Tri amido, Amyl., Bromo, Bromo iodo., Bromo nitro., Chloro, Chloro MITTO-, IODO, IODO NITRO, NITRO, DI OXY, ME THYL-, ETHYL , PROPYL , PHENYL , and BENZYL NAPHTHALENES Also NAPHTHOL, NAPHTHYLAMINE and Naphthylene DIAMINE

NAPHTHALENE, CONSTITUTION OF, vDICTIONARY OF APPLIED CHEMISTRY

NAPHTHALENE ALDEHYDE v NAPHTHOIC ALDEHYDE

NAPHTHALENE-DIAMINE v NAPHTHYLENE-DIAMINE

NAPHTHALENE-ARSONIC ACID v Organic compounds of Arsenic

NAPHTHALENE-AZO compounds v Azo

COMPOUNDS and Drs AZO COMPOUNDS
NAPHTHALENE CARBOXYLIC ACID v

NAPHTHOIC ACID

Naphthalene Peri-dicarboxylic acid C12H8O4 ve C_{1e}H_e(CO,H)₂ [1 1'] Naphthalic acid Mol w 216 [266°]

Formation -1 By oxidising acenaphthene with K₂Cr₂O, and H₂SO₄ or HOAc (Behr a Dorp, B 6, 852, A 172, 266, Anselm, B 22, 869) — 2 By oxidising pyrene ketone with KMnO₄ (Bamberger a Philip, B 19, 3040) -3 Bysaponification of its semi nitrile C, H, Cy CO2H which is formed by the action of cuprous cyanide upon diazotised peri amido naphthoic acid (Bam berger a Philip, B 20, 248 -4 By oxidising di-exo-oxy-acenaphthene with alkaline KMnO (Ewan a Cohen, C J 55, 580)

Properties -Long silky hair like needles (from alcohol), almost insol water, sl sol ether Split up into water and its anhydride by heating alone at 145°, by boiling with HOAc, or even by exposure over H SO, (Blumenthal, B 7, 1092) Distillation with lime yields naphthalene Yields a fluorescein on heating with resorcin

Salts -(NH₄)₂A"EtOH Plates (from al cohol) -Na₂A" -K₂A"EtOH Plates -BaA"aq Plates (from al sparingly soluble white silvery plates-CaA"aq

Di-methylether Me,A" [103°]

C10H < CO >0 Anhydride [266°] Needles (from alcohol), sl sol alcohol and benzene Not attacked by boiling HNO.

Imide C,H CONH [above 280°].

Formed by boiling the acid or its anhydride with aqueous ammonia White needles Sol warm When AgNO₃ is added to its solution KOHAq in alcoholic NH3 there is formed a crystalline pp Ag₂C₂₄H₁₅N₃O

Naphthalene dicarboxylic acid $C_{10}H_8(CO_2H)$, [255°] Formed by reducing di-oxy naphthal ene dicarboxylic acid [162°] with HIAq and amorphous phosphorus (Claus a Meixner, J pr[2] 37, 8) Flocculent pp, insol water and ether, sol alcohol Yields naphthalene on dis tillation with lime —PbA" greyish white pp

Naphthalene 'a' dicarboxylic acid $C_{10}H_0(CO_2H)_2$ [2 2] Obtained by digesting its nitrile with HClAq at 200° (Ebert a Merz, B 9, 606) Long needles (from alcohol) Melts far above 300° V sl sol boiling benzene, toluene, and HOAc, m sol boiling alcohol Yields naph thalene on distillation with lime - CaA' 4aq minute needles, sl sol water -Ag₂A''

Nitrile C₁₆H₆(CN)₂ [268°] Formed by distilling naphthalene (a) disulphonic acid with White needles (by sublipotassium cyanide

mation), m sol boiling alcohol

Naphthalene ' & ' dicarboxylic acid C10H6(CO.H) [2 3'] Obtained in the same way as the 'a' isomeride, from naphthalene 'B' disul phonic acid (E a M) Short needles (from alcohol) Melts far above 300° Almost insol boiling benzene, toluene, and HOAc, m sol boiling alcohol— K_2A'' aq tufts of needles, e sol water—CaA'' 3½aq minute needles, almost insol water— Ag_2A'' minute needles,

Nitrile C₁₀H₆(CN)₂ [297°] Long needles (from HOAc) Almost insol boiling ether, al-

cohol, and benzene

Naphthalene (γ) dicarboxylic acid

C₁₀H₆(CO,H)₂. Obtained from its nitrile, which is formed by distilling with KCy potassium bromo naphthalene sulphonate (obtained by sulphonating (a) bromo naphthalene) (Darm stadter a Wichelhaus, A 152, 309, Z [2] 5, 571) Small needles, v sol alcohol, insol boiling water —BaA" 2aq crystalline grains

Nitrile C₁₉H₆(CN)₂ [204°] Thin needles,

sl sol alcohol and ether

Naphthalene (δ)-dicarboxylic acid NitrileC₁₀H_e(CN)₂ [236°] Obtained by distilling potas sium bromo naphthalene (a) sulphonic acid with KCy (D a W) Needles, v sol alcohol

Naphthalene (ϵ)-dicarboxylic acid Nitrile $C_{10}H_{\bullet}(CN)_2$ [170°] Obtained by distilling potas sium bromo-naphthalene (B) sulphonate with KCy (D a W) Small needles, v sol alcohol Naphthalene tri-carboxylic acid

C₁₀H_s(CO₂H)₃ Obtained by quickly heating the tetra carboxylic acid to 200°-250° (Bamberger

a Philip, B 19, 3037)

Naphthalene tetra carboxylic acid C1.H.O. re C₁₀H₄(CO₂H), [1 1' 4 4'] Formed by oxidising pyrenic acid with dilute KMnO, (Bainberger a Philip, B 19, 1998, 20, 368, A 240, 182) Colourless glistening plates or needles, m sol hot HOAc and water, v sl sol alcohol and benzene Not attacked by HNO, even at 160° Yields naphthalene on distillation with lime —Ba₂A¹▼ (dried at 130°) --Ag₄A¹▼

Anhydride C₁₀H, ($\stackrel{CO}{<}$ 0)_r Formed by heating the acid at 150°-170° (Bamberger a Philip, B 19, 3037) Needles (from HOAc). Sublimes above 300° Gives a fluorescein when heated with resorcin

Imide $C_{10}H_4(\langle CO \rangle NH)$ Formed by treating the anhydride with NH, Aq Needles and prisms Sublimes in needles above 270° V sl sol alcohol, ether, and banzene Aqueous NaOH colours it yellow (forming the Na salt), without dissolving it, on adding acids it turns

Naphthalene dihydride dicarboxylic acid C₁₀H_s(CO₂H)₂ Dihydronaphthalic acidFormed by reducing naphthalic acid with sodium amalgam (Anselm, B 22, 859) Colour less crystalline solid, v sol warm alcohol, sl sol ether and water Reduces alkaline KMnO. It turns yellow at 150°-160°, froths at 199°, and changes to the anhydride, but is not melted at

Naphthalene tetrahydride dicarboxylic acid $_{\text{c}_{\text{e}}\text{H}_{\text{4}}}$ < $_{\text{CH}_{\text{2}}\text{CH}(\text{CO}_{\text{2}}\text{H})}^{\text{CH}(\text{CO}_{\text{2}}\text{H})}$ >When an [199°] alcoholic solution of ethane tetra carboxylic ether $C_2H_2(CO_2Et)_4$ (1 mol) and NaOLt (2 mols) is heated at 130° with di ω bromo o xylene $C_0H_4(CH_2Br)$ (1 mol) there is formed naph tetrahydride tetracarboxylic ether thalene C₈H, CH₂ C(CO Lt), and when this is sapo mified with alcoholic potash it loses CO2 (2 mols) yielding the dicarboxylic acid The yield is 70 pc of the theoretical (Baeyer a Perkin, B 17, 448, C J 53, 11) Minute tables, sl sol cold, m sol hot, water, v sol chloroform, al cohol, ether, and acetone Splits up at its melt ing point into H_iO and its anhydride On pass ing through a 1cd-hot tube it yields naphthalene -Ag,A" white crystalline pp which yields the anhydride and naphthalene on dry distillation

Anhydride C.H. CH2 CH CO

Four sided prisms (from ether) or needles (by sublimation), sl sol ether, m sol alcohol and chloroform, insol cold water Slowly re con verted into the acid by hot water Naphthalene tetra hydride tetra carboxylic

 $C_{e}H_{4} < \frac{CH_{2}}{CH_{2}} \frac{C(CO_{2}H)_{2}}{C(CO_{2}H)_{2}} > \frac{CH_{2}}{C(CO_{2}H)_{2}}$ Tetrahydro naphthalene tetracarborylic acid The ether is formed by heating an alcoholic solution of sodio chloro malonic ether CNaCl(CO,Et), (2 mols) with o xylylene bromide (1 mol), reducing the resulting CoH4(CH2 CCl(CO Et)2)2 by means of zinc dust and HOAc to o xylylene di malonic ether C₂H₄(CH CH(CO₂Et)₂)₂, and treating the sodium derivative C₂H₄(CH₂CNa(CO₂Et)₂)₂ with an ethereal solution of iodine (Baeyer a Perkin, jun, B 17, 448) The ether may also be obtained C₆H₁(CH₂Br)₂, sodium ethylate from C₂H₂(CO₂Et), (v supra) The free acid, which may be obtained by careful saponification of the ether with alcoholic potash, is a syrup which splits up at 185° into CO2 and the dicarboxylic acid described above

Reference - Bromo naphthalene dicarboxy LIC ACID

DI-NAPHTHALENE OXIDE v DINAPHTHYL ENE OXIDE

NAPHTHALENE DI-OXIM v Di-oxim of NAPHTHOQUINONE.

NAPHTHALENE - DIPHENYL AZAMMO. NIUM HYDRATE v AZAMMONIUM COMPOUNDS

ACID NAPHTHALENE PHOSPHINIC C₁₀H, P(OH)₂ Naphthyl phosphorous acra [126°] S G 1 377 (Schroder, B 12, 564) Formed by the action of water on its chloride Aggregates of small needles, sl sol cold water, almost insol HClAq Melts under water It is accompanied by an duces silver solution

duces shiver solution and the water ship and (C₁₀H₁)₂PO OH [204°] which is insol water.

Chlorade C₁₀H₁PCl₂ (above 360°) Formed by heating mercuric dinaphthyl Hg(C₁₀H₁)₂ orthogonal control of the ship and the PCl₃ at 190° for several hours (Kelbe, B 9, 1051, 11, 1499) Liquid Combines with chlorine forming C₁₀H,PCl,
NAPHTHALENE PHOSPHONIC ACID

C₁₀H, PO(OH), [190°] SG 1440 Formed by the action of water on its tetrachloride (Kelbe) Long needles, v sor nov, c. ____ water When strongly heated it decomposes, Long needles, v sol hot, sl sol cold, with separation of carbon, into naphthalene and metaphosphoric acid —Ag₂A" white pp Chloride C₁₀H,PCl₄ Formed from the

compound C10H,PCl2 and chlorine

NAPHTHALENE-STYRENE v NAPHTHYL

NAPHTHALENE (a) SULPHINIC ACID CaH SO H Formed by digesting a solution of the chloride of naphthalene (a) sulphonic acid in ether with sodium amalgam (Gessner, B 9, 1500, cf Otto a Mories, B 6, 860) White 1500, cf Otto a Mories, B 6, 860) White scales, v sol water, sl sol HClAq, m sol alco hol, sl sol ether Decomposed by HClAq at 180° into naphthalene and 50_2

Salts -KA' aq glistening scales -BaA' 1 aq Slender needles S 5 at 14°, 2 at 100° -PbA', aq long branched needles AgA' Soluble plates, not decomposed at 200°

Naphthalene (β)-sulphinic acid C₁₀H₇ SO₂H [105°] Formed in the same way as the preceding isomeride from naphthalene (8) sulphonic acid, and ppd by adding HCl to a solution of the Na salt as a white crystalline powder, m sol alcohol, ether, and water, almost insol HClAq Readily decomposed by HClAq at 150° into naphthalene and SO

Salts -KA' jaq scales -BaA', glistening needles S 4 7 at 15°, 6 25 at 100° -CaA', 3aq white crystalline solid, v sol water and alcohol -MgA'2 baq scales, more sol alcohol than water

References - Bromo and Chloro NAPHTHAL-ENE SULPHONIC ACID

(a) SULPHONIC ACID NAPHTHALENE C, H, SO, H Formed, together with the (B)isomeride, by dissolving naphthalene in H₂SO₄. At 160°-170° the chief product is the (β) acid, but at 80°-100° the product consists mainly of the (a) acid (Merz a Weith, B 3, 195, cf Faraday, P 7, 104, Berzelius, P 44, 377, Liebig a Wohler, P 24, 169, A 37, 197) Naphthalene is converted by Cl SO, H (1 mol) into a mixture of the (a) and (B) sulphonic acids (Armstrong, J 24, 173) It may be separated from the (B) isomeride by means of the calcium or lead salts Crystalline and deliquescent, v e sol water, sol alcohol, sl sol ether Partially converted into the (β) isomeride by heating with H₂SO, at 100°, more completely at higher tem peratures Decomposed into naphthalene and H2SO, by heating with HClAq at 200° Oxidised by KMnO, in acid solution to phthalic acid (Beilstein a Kurbatoff, C C 1881, 359, A 202, 216) Alkaline KMnO, yields C,H,(CO,H) CO CO,H (Henriques, B 21, 1607) and phthalic acid. Bromine forms dibromo naphthalene and bromo-

naphthalene sulphonic acid

naphthalene sulphonic acid

Salts—KA' ½aq Plates (from alcohol)

S 77 at 11°.—CaA' ₂aq Plates (slowly decomposed at 80°) S 6 at 11°.—BaA' ₂aq Plates

S 1 15 at 10° (M), 1 13 at 15°, 4 76 at 100°

(Regnault, J pr 12, 99)—PbA', 28aq Plates

S 37 at 10°.—Pb,OA', —AgA' S 10 3 at 10°

Ethyl ether EtA' Formed by boiling the selection of the selection

chloride (1 mol) with alcohol (2 mols) (Kimberly, A 114, 133) Viscid liquid, which slowly solidifies Insol water, miscible with alcohol and ether Decomposed on distillation, giving off SO, and naphthalene Aqueous or alcoholic potash merely saponifies it Water at 150° resolves it into alcohol, naphthalene, and H2SO4 Converted by PCl₅ at 160° into (a) chloro naphthalene and SOCl₂ (Carius, A 114, 145)

Chloride C, H. SO, Cl. [66°] Ghstening plates (from ether), v sol ether, CS, and benzene (Maikopar, Z 1869, 710, Kimberly, A 114, 129) On passing chlorine into a solution in CS, there is formed the tetrachloride O10H, Cl4 SO2Cl, a thick liquid, sol CS2, chloroform, benzene, and ether, and converted by alco holic potash into di chloro naphthalene sulphonic chloride (Widmann, B 12, 2228)

[150°] Amide C, H, SO, NH, by warming the chloride with cone NH, Aq Bol water, v sol alcohol and ether Its alco holic solution gives with AgNO, a crystalline pp C10H, SO2NHAg, v sol alcohol and ether,

quickly blackening in light

Benzoyl derivative of the amide H, SO₂NHBz [195°] Formed by heating C₁₀H, SO₂NHBz the amide with BzCl (Kimberly) Minute four sided prisms (from alcohol) (Wolkoff, Z 1871, 422, B 5, 142) Insol water, m sol alcohol and ether Decomposed by boiling KOHAq into benzoic acid, NH3, and naphthalene sulphonic acid PCl, converts it into C, H, SO, N CCl C,H, which crystallises from ether in large four sided plates [94°] and is re converted by boiling water or alcohol into C₁₀H₇ SO₂ NH COC₆H₃, and carbonate into crystalline ammonium C₁₀H, SO₂ N C(NH₂)C₆H. Behaves like an acid, decomposing carbonates, and forming the salts -C₁₀H, SO₂ NKBz prisms, v sol water and alcohol -CaA'₂ aq needles -BaA'₂ slender needles, sl sol water -AgA' minute needles

Anilide C₁₀H, SO₂NHPh [112°] Needles (Carleson, Bl [2] 27, 360)

(a) - Naphthalide Small needles (C) C10H, SO2 NHC10H,

Naphthalene (β)-sulphonic acid $C_{10}H$, SO_3H Produced by the action of H₂SO₄ upon phenyl (a) naphthyl ketone, the isomeric change result ing from the heat evolved in the reaction (Elbs a Steinike, B 19, 1966) Prepared by heating naphthalene (500 g) with H₂SO₄ (400 g) for 8 hours at 160° and purifying the acid by means of the Casalt (Merz a Weith, B 3, 196) Nondeliquescent crystals Not decomposed by dilute HClAq at 200° Split up into naphthalene and H.SO, by distilling with dilute H₂SO, at 135° in a current of superheated steam (Armstrong a Miller, C J 45, 148) Oxidased by alkaline KMnO, to C,H,(CO,H) CO CO,H | CaA''3aq (from a rapidly-cooled hot saturated

(Henriques, B 21, 1607) KMnO, in neutral or acid solution yields phthalic acid (Beilstein a Kurbatoff, C C 1881, 859, A 202, 215) OrO, and dilute H.SO, yield naphthoquinone sulphonic acid (B a K) The Ca salt yields phthalic acid on oxidation by CrO, Bromine water forms bromo naphthalene sulphonic acid

Salts—KA'şaq Plates (from water) or needles (from dilute alcohol) S 6 6 at 10° S (85 pc alcohol) 9—CaA', Plates S 13 at 10°—BaA', aq Plates S 345 at 10°—

PbA'213aq Scales S 9 at 10°

Chloride C10H, SO2Cl [76°] Plates, less soluble in ether than the (a) isomeride (Maiko par) Reduced by HI to (β) di naphthyl di sulphide [189°] (Cleve, B 21, 1100) Combines Combines with chlorine (dissolved in CS2) forming a tetrachloride C10H,Cl4SO2Cl, which separates from chloroform in colourless cubes [131°], v sol chloroform, CS, and hot HOAc, insol water (Widmann, B 12, 959) The tetrachloride is converted by boiling alcoholic KOH into di chloro naphthalene (B) sulphonic acid

Amide C10H, SO2NH2 [212°] (Cleve, Bl [2] 25, 258) Small thin plates (from alcohol), sl sol water and ether

Ethylamide C₁₀H, SO₂NHEt [82 5°] (Carleson, Bl [2] 27, 360)

Anilide C10H, SO2NHPh [132°] Needles (a) - Naphthalide C10H, SO, NHC10H [177 5°] Needles

Naphthalene tetrahydride sulphonic acid C₁₀H₁₁SO₃H Formed by heating naphthalene Graebe a Guye, B 16, 3030, Bamberger a Kitschelt, B 23, 1565) Crystals, v sol water and alcohol Decomposed by distillation with dilute H₂SO₄ and a current of superheated steam at 175° , or by dilute H₂PO, at 130° (Finedel a Crafts, Bl [2] 42, 66, CR 109, 95) — NaA'2aq Tables, v sol water —BaA'2aq Tables, sol hot alcohol, sl sol cold water

Naphthalene 'a'-disulphonic acid

C₁₀H₆(SO₃H), [2 2] Formed, together with about O₁₀H_c(SO,H)₁[2] Formed, together with about an equal quantity of the (β) isomeride and some of the (δ) isomeride, by heating naphthalene (1 pt) with H_cSO₄ (5 pts) for 4 hours at 160° (Ebert a Merz, B 9, 592, Armstrong, B 15, 204, cf Berzelius, A Ch [2] 65, 290, Laurent, Compt. Chim. 1849, 390) The acids may be contributed to the contribute of the contribute o partially separated by their Ca salts, that of the (B) acid crystallising out first, while that of the (a) acid is the most soluble The potassium salt of the (a) acid is more soluble than that of the (β)- acid, and less soluble than that of the (δ) acid Long, very deliquescent needles, sl sol cold conc HClAq Gives di oxy naphthalene [186°] on fusion with KOH (cf Griess, B 13, 1959, Dusart, C R 64, 859, Darmstadter a Wichelhaus, A 152, 306) Water at 200° splits NaOH forms (β) naphthol (δ) sulphonic acid C₁₀H₆(OH)SO₂H (Weinberg, B 20, 2906) PBr₆ forms (8)-d1-bromo naphthalene Yields di-

chloro-naphthalene [114°].
Salts — K₂A" 2aq Transparent needles (from hot saturated solutions). S (of K₂A") 71 at 18° —Na₂A"6aq Ghistening needles S (Na₂A") 45 5 at 18° —CaA"6aq S 16 at 18°

solution) —BaA"2aq Long, broad needles S
1 2 at 19° —PbA"2aq Long needles, sol water

Chloride $C_{10}H_6(SO_2Cl)_2$ [158°] (E a M), [162°] (A) Obtained by heating the K salt with PCl_s at 140° Plates (from benzene), or needles Plates (from benzene), or needles (from ether) S (benzene) 18 3 at 14° Amade C₁₀H₆(SO₂NH₂)₂ [243°]

[243°] Needles.

m sol hot NH_3Aq and alcohol
Naphthalene ' β '-disulphonic acid $C_{10}H_4(SO_3H)_2$ [2 3']? Almost the sole pro

C₁₀H₅(SO₃H)₂ [2 3']? Almost the sole product obtained by heating a mixture of naphthal ene (1 pt) and H₂SO₄ (5 pts) for 24 hours at 180° (Ebert a Merz) Formed also from its 'a'-isomeride by prolonged heating with H2SO. at 180 Somewhat deliquescent plates (β) naphthol 'β' sulphonic acid and (β) di oxynaphthalene on fusion with potash Yields C₁₀H₆Cl [135°]

Salts —Na,A"aq aggregates of minute prisms S (of Na,A") 1 2 at 19° —K,A" Bushy groups of needles S 5 2 at 18° —CaA"aq S 6 2 at 18° When once dry this salt dissolves in

water with great difficulty - Bah"aq — Pbh"aq Chloride C₁₀H_s(SO₂Cl)₂ [226°] S (benz ene) 45 at 14° Tufts of small needles or thin plates, v sl sol HOAc (difference from the (a)isomeride), v sol benzene

Amide C₁₀H₆(SO₂NH₂) Small needles, v sl sol NH, Aq, almost insol alcohol, ether, benzene, and toluene Not melted at 305°

Naphthalene (γ) disulphonic acid $C_{10}H_6(SO,H)$, [1 4'] Formed by treating naph thalene (1 mol) with ClSO3H (2 mols) below 100° and also by sulphonating naphthalene with SO, (Armstrong, B 15, 204, Armstrong a Wynne, C J Proc 2, 230, 3, 42) Its Pb, Ca, and Ba salts resemble those of the (β) acid, dissolving very sluggishly in water On fusion with potash it yields di oxy naphthalene [260°] -Na,A" 2aq -K,A" 2aq plates, less soluble than the corresponding salt of the 'a' acid Chloride CiaH, (SO Cl) [184°] Pr

Chloride C₁₀H₁(SO Cl) [184°] Prisms (from benzene) Yields (γ) di chloro naphthal ene [107°] on treatment with PCl,

Naphthalene (δ) disulphonic acid

 $C_{10}H_{b}(SO_{3}H)$ [1 3'] Also called (γ) Occurs in sniall quantity in the product of sulphonation of naphthalene by H SO, at 160° (Armstrong, B Formed by treating potassium naph thalene (3) sulphonate with ClSO3H (Armstrong a Wynne, C J Proc 2, 230) - BaA '4aq Formed also by heating naphthal-NaA' 7aq that 124 Tollied also by leading H₂SO₄ at 100° (Ewer a Pick, & P 45,229 [1887], Aim strong, & J Proc 4, 10) Long needles Gives dioxy naphthalene [1355°] on fusion with potash Yields C₁₀H₂Cl₂[49°] The potassium salt is more soluble than that of the (a) or (β) acid — $K_2A''aq$ — $Na_2A'' 4aq$ — BaA' 4aq — CaA" 4aq -PbA"32aq

Chloride CloH_s(SO₂Cl) [125°] Small prisms (from benzene) On treatment with PCl, it yields di chloro naphthalene [59°

Naphthalene (1, 2') disulphonic acid Formed from (a) naphthylamine disulphonic acid (Armstrong a Wynne, C J Proc 5, 136) $C_{10}H_{\alpha}Cl_{2}$ [62 5°] $-K_{1}A''$ aq

Chloride [122 5°]

Naphthalene (1, 3) disulphonic acid tained from (1', 1, 3) or (2, 2', 4') naphthylamine disulphonic acid by eliminating NH2 (Armstrong

a Wynne, C J Proc 5, 18, 129) C₁₆H₅Cl₂ [61°] - K₂A" 2aq --BaA" 4aq Yields Chloride [137°]

Naphthalene hexahydride (α)-di-sulphonic acid C₁₀H₁₂(SO₃H). Formed by heating naphthalene hexahydride with H₂SO₄ and SO₄, and separated from the (3)-isomeride by means of the K salt (Agrestini, G 12, 495) -KA" (dried at 105°) Nodules, sol alcohol

Naphthalene hexahydride (β)-sulphonic acid C10H12(SO3H)2 Formed as above -

K₂A" 1½aq Insol alcohol.

Naphthalene trisulphonic acid CieHs(SOsH), 242. Formed from naphthalene and ClSO₃H (Wynne, C J Proc 3, 146) [194°] —Na, A'''5aq Yields C, H, Cl,

Naphthalene tetra-sulphonic acid

C₁₀H₄(SO₃H)₄ Formed by heating naphthalene with H.SO, and PO, for three or four hours at 260° (Stenhofer, B 8, 1486, M 3, 111) Two isomeric acids are formed in the process, and when a solution of their Ba salts is slowly evaporated at 30° to 35° the salt of the acid here described crystallises out in striated prisms Prisms (containing 4aq), v e sol water, sl sol alcohol, insol ether Decomposes above 170°

Salts —K,A'v 2aq non deliquescent needles -Na,A'v 2aq (at 100°) — Na,A'v 10aq very de liquescent prisms — Ba Aiv xaq prisms -Pb Aiv 6aq crystalline pp -Cu, Aiv 12aq blue prisms - Ag, Aiv 2 aq very soluble needles

References - BROMO , CHLORO , IODO- and

NITRO NAPHTHALENE SULPHONIC ACIDS

NAPHTHAL-FLUORESCEIN C24H14O5 Se by heating naphthalic anhydride and resorcin at 250° (Terrisse, A 227, 136) Yellow rhombic prisms Its alkaline solution is red, with splendid green fluorescence

Acetyl derivative C.H., Aco, [1910] C₂₄H₁₈AcO₃aq [120²] Needles (from acetone) Insol alkalis, but saponified slowly By treat ment with PCl, it is converted into the chloride C H12O,Cl, which crystallises in scales, sol chloroform, acetone, or glacial acetic acid, hardly sol benzene, ether, or alcohol

Naphthal eosiu $C_{24}H_{16}Br_4O_5$ [above 310°] Formed by adding bromine to an alcoholic solution of naphthal fluorescein Its alkalıne solutions are orange, with yellow fluorescence, and dye silk scarlet

NAPHTHALIC ACID v Naphthalene di CARBOXYLIC ACID

NAPHTHALIDES Alkoyl derivatives of Naphthylamine $(q \ v)$

NAPHTHALIDINE SULPHONIC ACID v. (1,4') NAPHTHYLAMINE SULPHONIC ACID

NAPHTHALIN v NAPHTHALEND

(B) NAPHTHAMIDINE C₁₀H, C(NH) NH, White crystalline mass, obtained from its hydrochloride, which is prepared by the action of alcoholic NH, at 50° to 60° upon (\$) naphthimdo ether C₁₀H, C(NH) OEt (Pinner a Klein, B 11, 1486)—B'HCl [226°] Needles

(a) NAPHTHAMIDOXIM C₁₁H₁₀N₂O s.e.

O₁₀H, C(NOH) NH₂ [149°] Obtained by mixing the nitrile of (a) naphthoic soid with hy-Obtained by mixdroxylamine hydrochloride, Na₂CO₂, and alcohol (Ekstrand, B 20, 223) Plates (from dilute alcohol), v sol alcohol, insol ligroin On boiling with Ac_2O it yields $C_{10}H$, C < NO > CMe[36°] ClCO₂Et yields C₁₀H, C(NO CO₂Et) NH₂ COCI, forms C₁₀H, C NO CO [189°] (Richter, B 22, 2458) -B'HCl [160°] Needles —B',H,PtCl, yellow prismatic needles Acetyl derivative C₁₀H,C(NOH) NHAc [129°] (Richter, B 20, 227) White needles,

insol water, v sol alcohol and ether (a) Naphthoyl derivative C₂₂H₁₆N₁O₂ re C₁₆H, C(NOH) NH CO C₁₆H, [228°] Needles,

almost insol HClAq

C₁₀H, C(NOH) NH₂ (β) Naphthamidoxim Formed from (3) naphthonitrile and [150°j alcoholic hydroxylamine (Ekstrand) Scales, decomposed by boiling water On heating with Ac,O it yields C₁₀H, O < N > OMe [86°], which is also formed by boiling the acetyl derivative with water (3) Naphthoyl chloride forms the corresponding azoxim $C_{10}H_{7} \ll_{N}^{N} > C C_{10}H_{7}$ Acetic aldehyde yields the compound C10H, C NH CH CH, [122°] crystallising in needles Cyanogen passed into an alcoholic solution of (8) naphthamidoxim forms the com C, H, C(NOH) NH C(NH) CN (Bruhl, B 23,1463) ClCO, Et in chloroform forms C₁₀H, C(NO CO, Et) NH, crystallising in needles [121°] COCl₂ yields white felted needles of $C_{10}H$, C < N O > CO [216°] Boiling acetoacetic

ether forms $C_{10}H_7 C \gtrless_N^{N}O > C CH_2 CO CH_3 crys$

tallising in plates [109°]
Salt —B'HCl [178°] Needles, v sol water Acetyl derivative C₁₀H, C(NOH) NHAc [154°] Faintly yellow needles, insol water, sl sol cold alcohol and ether

Benzoyl derivative C10H, C(NOH) NHBz [179°] Silky felted needles (from alcohol), in sol water, sl sol cold alcohol On boiling with water it yields $C_{10}H$, $C < N O > C C_6H$, [116°]

Ethyl ether C10H C(NOEt) NH, Formed from (\$\beta\$) naphthamidoxim, NaOEt, and EtI at 100° (Richter, \$B\$ 20, 227, 22, 2455) Shining felted needles, v sl sol water, v sol alcohol, ether, chloroform, and ligroin, sol HClAq, insol NaOHAq

NAPHTHANISOL v Methyl ether of NAPH THOL

NAPHTHANTHRACENE C18H12 t.6

 $C^eH^* < CHCHCH > C^eH^*$ [141°] Formed by boiling naphthanthraquinone with zinc dust and aqueous NH3Aq till the red colour has dis appeared, extracting the residue with alcohol and adding HOAc to the extract (Elbs, B 19, Large colourless serrated plates with powerful green yellow fluorescence May be sublimed — Piorate C₁₈H₁₂2C₆H₂(NO),0H May be [133°] Red needles (from benzene), decom posed by alcohol

NAPHTHANTHRAQUINONE C18H10O2 8.6 C₆H₄<CO>C₁₀H₆ [168°] Formed by heating naphthoyl o benzoic acid with conc. H2SO4 (Elbs. |

B 19, 2209) Glittering deep fellow grains or prisms, sl sol alcohol and ether, m sol acetone, HOAc, and EtOAc, v sol chloroform and bonzene, insol petroleum ether May be sub-limed as needles arranged in leaflets Cone H2SO, forms a brown solution Sodium amalgam added to its alcoholic solution forms a darkviolet zone (like anthraquinone), but on warming the liquid becomes red (anthraquinone gives a green liquid) It does not combine with picric acid

NAPHTHAQUINOLINE v NaPHTHOQUINOL

NAPHTHAQUINONE v NAPHTHOQUINONE NAPHTHAZABIN v DI - OXY NAPHTHO QUINONE

(αβ) NAPHTHAZINE $C_{20}H_{12}N_2$ ι ε

C.H. CH CH CN C CH CH CH, Naphthase [275°]

Formation -1 By heating (a) nitro naph thalene to redness with lime (Laurent), or zinc dust (Doerr, B 3, 291, 10, 772, Klobu lowski, B 10, 570) -2 By the action of (β) naphthoquinone in HOAc solution upon naph thylene o diamine (Witt, B 19, 2795) -3 By fusing (3) naplithoquinone with ammonium accetate, the yield being small (Japp, C J 51, 100) -4 By heating (a) chloro (b) naphthyl amine with lime (Cleve, B 20, 1991)

Properties - Yellow needles, sl sol alcohol

and benzene, with pale violet fluorescence, m sol phenol and aniline Conc H₂SO₄ forms a violet solution becoming orange yellow on dilu tion, and finally colourless, depositing the naph thazine Bromine in presence of iodine yields C₂₀H₂Br₄N₂ melting above 320°

(ββ) Naphthazine CeH CH CN C CH CH CH

Formed by adding a strongly acid solution of diazobenzene chloride to a warm solution of $(\beta\beta)$ di naphthylamine (Matthes, $B=23,\ 1333)$ Woolly bunches of long yellow needles (from hot alcohol or hot HOAc) Its solutions in alcohol and benzene exhibit a blue fluorescence, its solution in HOAc shows green fluorescence

NAPHTHENES C_nH _n A class of hydro carbon, forming the principal constituents of Caucasian petroleum, they are isomeric with the olefines, from which they differ in behaving as saturated compounds They resemble the paraffins in yielding by substitution chloro derivatives, readily dissociated into hydrochloric acid and a hydrocarbon of formula C_nH_{2n-2} oxidation they are converted into hydrocarbons poorer in hydrogen and oxygenated products, thus resembling naphthalene

As regards their constitution the carbon atoms are arranged in a closed chain, and the determination of the specific refractive energy of the members of the series appears to show that they contain no olefinoid combination of carbon atoms They are probably hexahydrides of the aromatic hydrocarbons

They also probably occur in petroleum from Hanover, Galicia, Borislau, and Burmah, but have been mistaken by former observers for the olefines They are also formed in the dry distillation of resin (cf. Renard, C. R. 95, 141, 243).

The following are the physical properties of some of the members examined

	SC 16-18	με	μρ	μγ	μD	R.
Decanaphthene Endecanaphthene Dodecanaphthene Tetradecanaphthene Pentadecanaphthene	. 7808 . 8019 . 812 . 8215	1 43000 1 43883 1 4438 1 44913 1 4544	1 43863 1 4466 1 45173 1 45706 1 46136	1 4427 1 45156 1 45646 1 4619 1 4661	1 433 1 441 1 44606 1 4514 1 4544	77 2 84 2 91 8 107 1 114 7

The naphthenes are obtained from the following fractions of Caucasian petioleum

Octonaphthene CaH16	116 -120°
Nonaphthene C.H.	1∃5°-140°
Decanaphthene C ₁₀ H ₀	1 > 5° - 16 5°
Endecanaphthene C11H22	140°-185°
Dodecanaphthene C12H24	196°-1 97°
Tetradecanaphthene C14H26	240 241°
Pentadecanaphthene C1.H.	246° 248°
Markownikoff a Oglobine A	Ch. [6] 2, 446)

Some of these hydrocarbons (eg octonaph thene and nonaphthene) occur in two isomeric forms. Octonaphthene on treatment with HSO₄ and HNO₃ yields tri nitro m xylene, and it is therefore probably m xylene hexahydride (Markownikoff a Spady, B 20, 1851). Nonaphthene (136°), S G % 7667 is identical with pseudo cumene hexahydride, for it yields some tri nitro \(\psi\$ cumene on intrition and \(\psi\$ cumene sulphonic acid with excess of HSO₄ (Konovaloff, C C 1887, 1133, J R 22, 4, 118). Heptanaphthene C₇H₁₄ also occurs in Caucasian petroleum and boi's at 101° (Milkow k), bl [2] 45 182)

Hexanaphthene carboxylic acid C₀H₁₁ CO H
Hexanydro benzoic acul? (216°) S G 124 4
9503 Obtained from the oils of Baku by extracting with caustic soda, and puinted by fiactional distillation of its methyl ether (Aschau, B 23, 867) Thick colourless oil, smelling like valeric acid Not solid at -10° Not attacked by bromme in the cold HNO, and kMnO, act slowly upon it It slowly expels HCl from CaCl₂ Cone HSO, dissolves it, and, on warming, decomposes it Phosphoric acid decomposes it gradually in the cold

Salts—KA Very hygroscopic soap like mass, gradually becoming crystalline, v sol water and alcohol—NaA' Flat hygroscopic prisms—CaA' 4aq long pointed needles A saturated solution becomes milky on heating and clear again on cooling—BaA. Large thin plates, v sol alcohol, m sol water—BaA', 2aq Amorphous—CdA', Pearly plates, sl sol cold water—AgA' Curdy pp

Methyl ether MeA' (167°) SG $\frac{18}{18}$ Golourless liquid with sickly odour

Chloride C.H., COCl (168°) Slowly de composed by water

Amide C₆H₁₁ CONH₂ [123 5°] Melts under water Extremely thin pearly plates, m sol water, v sol other solvents

Antitale C₃H₁₁ CO NHPh [94°] Long elastic needles

NAPHTHENYL-AMIDINE v Naphthauid

NAPHTHIDINE v Di amido dinaphthyl.
NAPHTHIL BENZOIN v BENZOIN

(β) NAPHTH IMIDO-ACETATE C₁₂H₁₁NO₂ i e C₁₀H, C(NH)(OAc) [152°] Prepared by boiling naphth imido isobutyl ether with Ac₂O (Pinner a Klein, B 11, 1487) White needles.

(β) NAPHTH-IMIDO-ISOBUTYL ETHER C.,H. NO ie C., H., C(NH) OC.,H., [38°]. Pre pared by the action of gaseous HCl on a solution of (β) naphthomitrile C., H., CN in isobutyl alcohol (Pinner a Klein, B 11, 1487) Long white needles—B HCl Decomposed by heat into isobutyl chloride and the amide of (β) naph thoic acid

(β)-NAPHTHIMIDO ETHYL ETHER

C₁₀H C(NH) OEt Hydrochloride B'HCl

Prepared by leading HCl into an alcoholic solution of the intrile of (β) naphthoic acid (Pinner a. Klein, B 11, 1485) Decomposed by heat into EtCl and the amide of (β) naphthoic acid

(a) NAPHTHINDOLE C₁₂Ĥ₉N 1 e

C₁₀H₆<0H CH [175°] Obtained by distil

ling its carboxylic acid (Schlieper, A 239, 229) Plates (from ligroin), v sol alcohol, ether, and benzene, sl sol hot water Colours pine wood, in presence of HCl, blush violet Its solution in acetic acid gives a red colour with cone HNO, and a blush green pp on boiling with hydrogen peroxide Its pictate crystallises in needles—B'aHCl Colourless pp, got by adding HCl to the solution in HOAc

On boiling an alcoholic solution of (α) naphthindole with zinc dust and HCl there is formed a hydride which yields an oxalate melting at 106°

(8) Naphthindole $C_{10}H_{\bullet} < {\rm CH \atop NH} > {\rm CH}$ (above

360°) at 760 mm , (222° 1 V at 18 mm)

Formation —1 By heating ethylidene (β)
naphthyl hydrazine with ZnCl₂, the yield being
small —2 By heating the (β) naphthyl hydraz
ide of pyruvic ether with ZnCl₂ at 195°, the
intermediate body being (β) naphthindole car
boxylic acid (Schlieper, A 236, 178)

Properties — Yellow oil, v sol alcohol, ether, benzene, and HOAc, sl sol ligroïn Yields a picrate, crystallising in dark red needles, and a nitrosamine Cone HClAq solidines the oil It colours pine wood, in presence of HCl, violet Oxidising agents yield a solid product

(a) NAPHTHINDOLE CARBOXYLIC ACID $C_{13}H_9NO_2$ se $C_{19}H_6 < \stackrel{CH}{\sim}_{NH} > CCO_2H$ [202°]

Formed by the action of boiling alcoholic potash upon its ether, which is obtained by heating the (a) naphthyl hydrazide of pyruvic ether with ZnCl₂ (Schlieper, A 239, 232) Silvery lamina (from water), v sl sol hot water, v sol alcohol and ether Decomposes above 210° into CO₂ and (a)-naphthindole

Ethyl ether EtA' [170°] (β)-Naphthindole-carboxylic acid C, H, NO2 i.e C₁₀H_e CH CO H [226°] Obtained by

saponifying its ether, which is formed when the (8)-naphthyl hydrazide of pyruvic ether is heated with ZnCl₂ (Schlieper, A 236, 181) Colourless Colourless plates, insol water, sl sol ether, v sol hot Does not colour pine-wood HOAc and alcohol Bromine gives a yellow pp
(a)-NAPHTHINDOLE

SULPHONIC ACID

 $C_{10}H_6 <_{CH}^{NH} > C SO_3H$ (?) The sodium salt of this acid, formed by the action of (a) naphthyl mine on the compound of glyoxal with NaHSO3, s converted by mineral acids into (a)-naphthox ndole (Hinsberg, B 21, 116)

S-Naphthindole sulphonic acid

$$\mathtt{J_{10}H_{0}} \underset{\sim}{\overset{NH}{>}} \mathtt{C} \ \mathtt{SO_{3}H} \ \mathtt{or} \ \mathtt{C_{10}H_{0}} \underset{\sim}{\overset{N}{<}} \mathtt{C_{H_{2}}} \underbrace{\hspace{0.1cm}} \mathtt{C} \ \mathtt{SO_{3}H}$$

The sodium salt of this acid is obtained by the ection of (β) -naphthylamine on the compound of glyoxal and NaHSO₃ (Hunsberg, B 21, 113) t is stable towards alkalis, but converted by

nineral acids into (β) naphthoxindole NAPHTHIONIC ACID v (1, 4) NAPHTHYL-

MINE SULPHONIC ACID.

NAPHTHISATIN v ISATIN

NAPHTHOACRIDINE v NAPHTHACRIDINE NAPHTHOBENZALDOXIM so called, v Oxim of Naphthoic aldehyde

NAPHTHOBENZYL ALCOHOL v NAPHTHYL JARBINOL

NAPHTHOBENZYLAMINE v NAPHTHYL-

NAPHTHO-CINNAMIC ACID so called, v

NAPHTHYL ACRYLIC ACID NAPHTHOCOUMARIC ACID Oxy NAPHTHYL-ACRYLIC ACID

NAPHTHOCOUMARIN v Anhydride of Oxx-NAPHTHYL ACRYLIC ACID

NAPHTHOCYAMIC ACID C29H18N8O, potassium salt of this acid is prepared by boiling di nitro naphthalene with alcoholic KCy (Muhl hauser, A 141, 214) The free acid is a brownish black mass, insol ether, nearly insol water, m sol alcohol -KA' aq Dark mass, with coppery lustre, forming a fine blue solution in hot water and hot alcohol The barrum salt is a dark blue pp, and explodes when heated The silver salt is insol water, has a bronze lustre, and explodes violently when heated

NAPHTHO-HYDROQUINONE Hydro-NAPHTHOQUINONE

(a) NAPHTHOIC ACID C,HO2 2.6 Naphthalene (a) carboxylic acid C, H, CO, H [162°] HCv 1,232,000 HCp Mol w 172 HF 77,400 (Stohmann, Kleber, a 1,232,600

Formation — I By saponifying its nitrile by boiling alcoholic potash (Merz, Z [2] 4, 34, 5, 396) or cone HClAq (Hofmann, B 1, 39) — 2 By heating a mixture of bromo-naphthalene and Cl CO2Et with sodium amalgam at 110° for several hours, and saponifying the resulting ether with alcoholic potash (Eghis, C R 69, 360) -3 By fusing potassium naphthalene (a). sulphonate with sodium formate (V Meyer, A 156, 274) -4 By boiling with potash its amide which is formed by the action of ClCO NH, on

naphthalene in presence of AlCl, (Gattermann, A 244, 56)

Preparation — A mixture of 3 pts of sodium naphthalene (a) sulphonate and 2 pts of potas sium ferrocyanide (both quite dry) is distilled from an iron tube, the nitrile is rectified and saponified by heating it with an equal volume of HCl to 200°, the yield is 25 p c of the sulphon ate (Boessneck, B 16, 639)

Properties - Needles (from dilute alcohol), v sl sol water, m sol hot alcohol Yields naph thalene on distillation with lime, and phthalic acid on oxidation by CrO, in HOAc

Salts—BaA'₂4aq Needles, sl sol water— CaA',2aq S 108 at 15°—AgA'

Ethyl ether EtA' (309° cor)

Chloride C₁₀H, CO Cl (297 5°) From the acid (4 pts) and PCl, (5 pts) Hydroxylamine converts it into C₁₀H, CO NH OH [187°] and (C₁₀H, CO)₂NOH [150°] (Ekstrand, B 20, 1358) Reacts with potassium (B) naphthoate, forming (aB) naphthoic anhydride C10H, CO O CO C10H (Hausmann, B 9, 1515)

Amids C₁₀H, CONH₂ [202°] Formed from the chloride and NH3, or from the nitrile and alcoholic soda (Hofmann, Ekstrand, J pr [2] 38, 146) Prepared by passing dry gaseous cyanic acid and HCl into a solution of naphthalene in CS, containing AlCl, heated on the water bath (Gattermann a Rossolymo, B 23, 1197) Colour less monoclinic tables (from alcohol) (Bamberger a Philip, B 20, 241)

Anilide C₁₀H, CONHPh [160°]

silky crystals

(a) Naphthalide [244°] C₁₀H CO NHC₁₀H Anhydride (C10H, CO) O [145°]

tained by distilling calcium naplithoate with naphthyl chloride (Hofmann) Prisms (from boiling benzene)

Nitrile C₁₀H, CN (a) Cyano naphthalone Mol w 153 [37°] (298° cor) Formation— 1 By distilling naphthylamine with oxalic acid and heating the resulting formyl derivative of naphthylamine with HClAq (Hofmann, A 142 121, B 1, 39) —2 By distilling potassium naphthalene (a) sulphonate with KCy (Merz, Bl [2] 9, 335, 10, 47) or K.FeCy, (Boessneck, B 16, 639, Hausmann, B 9, 1514) — 3 By passing a mixture of cyanogen and naph thalene through a red hot tube (Merz a Weith, B 10, 746)—4 By heating di naphthyl thio urea with copper powder (Weith, B 6, 967)— 5 By heating tri (a) naphthyl phosphate with KCy, the yield being 20 pc of the theoretical (Heim, B 16, 1779) -6 By boiling the formyl derivative of (a)-naphthylamine with zinc dust in a current of hydrogen, the yield being 11 pc (Gasiorowski a Merz, B 18, 1006) -7 By the action of cuprous cyanide on (a) diazo naphthalene salts (Bamberger a Philip, B 20, 257) Properties — Needles Reduced in alcoholic solution by sodium to the tetrahydride of naph thyl carbinylamine C₁₀H₁₁ CH₂NH₂ On heating with hydroxylamine it yields CieHii CONH, and naphthamidoxim [149°

(β)-Naphthoic acid C₁₀H, CO₂H Isonaphthoic acid [185° cor] (above 300°) H C v. 1,227,800 H C p 1,228,400 H.F 81,600 (Stohmann, Kleber, a Langbein, J pr [2] 40, 137)

Formation -1 By saponification of its

nitrile, which is formed by heating potassium asphthalene (β) sulphonate with KCy (Merz a Muhlhauser, Z [2] 5,70)—2 By boiling (β)nethyl naphthalene with conc HNO, (Ciamician, B 11, 272) -8 By oxidising (3) naphthoic ildehyde with KMnO, (Schulze, B 17, 1530)

Properties -Long white needles (from hot water), sl sol hot water, v sol alcohol and other Yields naphthalene on distillation with baryta Oxidised to phthalic acid by CrO, in

HOAc

Salts -NaA' aq (Vieth, A 180,314) Small tables, v e sol water — KA' 3aq —BaA' 4aq -Needles (from hot water) S 07 at 15° 055 at 15° - MgA', 5aq -CaA'₂ Baq AgA'

Methyl ether MeA' [77°] (290°) H.F

70,600 (Stohmann, J pr [2] 40, 353) Ethyl ether EtA' (309°)

Chloride C10H, COCI [43°] Formed from the acid and PCl, (Vieth, cf Grucarevic a Merz, B 6, 1242) Hydroxylamine solution at 100° attacks it, forming the compounds $C_{10}H$, CO NH OH [168°], and $(C_{10}H$, CO)₂NOH [171°] (Ekstrand, B 20, 1359) The (B) naph thoyl hydroxylamine reacts with (a) naphthoyl chloride forming (as) di naphthoyl hydroxyl amine [160°] With urea it forms di naphthoyl-urea [215°]

Anhydride (C10H, CO)2O [134°] composed of needles (Hausmann, B 9, 1515)

Amide C,0H, CONH, [192°] Formed by warming the chloride with powdered ammonium carbonate Formed also by heating the nitrile with alcoholic potash (Leone, G 14, 120) Plates

Anilide C₁₀H, CO NHPh [170°]

plates (from benzene)

p Tolurde CieH, CO NHC, H, [191°] Silky needles

(a) Naphthalide C₁₀H, CO NE [157°] Very small needles, sl sol ether C₁₀H, CO NH C₁₀H,

(305° coi) Nitrile C₁₀H, CN [66 5°] Formed by reactions like those used for prepa ring its (a) isomeride (v supra) White mass, nearly insol water, v sol alcohol and ether When its alcoholic solution is saturated with HCl there is formed the hydrochloride of naphthimido ethyl ether $(q \ v)$ (Pinner a Lohmann, B 11, 1485) By exhaustive chlorination with SbCl, it yields per chloro-benzene (Merz a Weith, B 16, 2887)

References - Amido-, Bromo , Bromo nitro CHLORO, CHLORO NITRO-, NITRO-, OXY, and THIO, NAPHTHOIC ACIDS, and AMIDO-, and BROMO-

AMIDO NAPHTHOIC ANHYDRIDE

(a) NAPHTHOIC ACID TETRAHYDRIDE C10H11 CO2H [128°] Formed, together with the amide, by heating its nitrile with alcoholic pot ash for 5 or 6 hours at 165° (Bamberger a Bordt, B 22, 629) Slender dendritic prisms, v sol alcohol, sl sol cold water —CuA'₂ bluish green pp —PbA'₂ needles grouped in stars —AgA' flaky pp

Amade C10H11 CONH2. [182°] Flat needles,

▼ sol boiling water

Natrale C, H, CN (278°) at 721 mm Formed from (a)-naphthylamine tetrahydride by Sandmeyer's reaction, and purified by steam-dis-

(a) NAPHTHOIC ALDEHYDE C,oH, CHO • Naphthobensaldehyde' Mol w 156 (292° cor)

Formed from naphthyl carbinol by oxidation with chromic acid mixture (Bamberger a Lodter, B. 21, 258) Pale yellow viscid liquid, with faint aromatic odour Conc HNO, at -5° yields a nitro-derivative [136°] It forms with NaHSO, a compound crystallising in glistering leaflets The phenyl hydrazide [185°] forms yellow leaflets. which turn red on exposure to light Aniline forms C₁₀H_cCH NPh [71°], o toluidine yields C₁₀H_cCH NC,H, [59°], p toluidine produces C₁₀H_cCH NC,H, [93°], and (α)-naphthylamine C₁₀H_cCH NC,H, [117°]

Oxim C₁₀H, CH NOH 'Naphthobenzaldoxim' [98°] Colourless needles (fron hol), sl. sol water (Brandes, B 22, 2151) Colourless needles (from alco-

(β)-Naphthoic aldehyde C₁₀H, CHO Formed by distilling a mixture of calcium (8) naphthoate and calcium formate at a high temperature (Battershall, Z [2] 7, 292, 673, A168, 116) Formed also by heating w chloro (β) methyl-naphthalene (C₁₀H, CH₂Cl) with lead nitiate (Schulze, B 17, 1530), and by oxidising (β)-naphthyl carbinol (Bamberger a Brekmann, B 20, 1118) Silvery plates, volatile with steam Reduces ammoniacal AgNO₃ Alcoholic NH₃ converts it into the hydramide (O_{1c}H₁, CH)₃N₂ [146°-150°]
(a)-NAPHTHOL C₁₀H₁ OH Mol w 144,

[949] (279°) SG 1 1 224 (Schröder, B 12, 1613) R₂₀ 76 97 in an 86 pc alcoholic solu tion (Kanonnikoff, J pr [2] 31 348), 75 25 (Nasını a Bernheimer, G 14, 153) Occurs in anthracene oil obtained from coal tar (K E

Schulze, A 227, 150)

Formation —1 By the action of nitrous acid on (a) naphthylamine (Griess, J 1866, 460) 2 From naphthalene (a) sulphonic acid by pot ash fusion (Eller, A 152, 275) -3 By heating γ phenyl isocrotonic acid CHPh CH CH, CO, H at its boiling point for 5 or 10 minutes, water being eliminated (Fittig a Erdmann, B 16, 43, A 227, 242)

Preparation —By heating naphthalene (1 pt) with H₂SO₄ (2 pts) at 60° to 70°, and fusing the sodium salt of the (a) sulphonic acid formed

with three times its weight of NaOH

Properties -Short trimetric prisms (Léger, C R 111, 110), sl sol hot water, v sol alco hol, ether, and benzene Volatile with steam Volatile with steam Pine wood, moistened with an aqueous solution of (a) naphthol, and then with HClAq, turns green in sunlight, and finally reddish brown Bleaching powder gives, in a solution of (a)naphthol, a dark violet colour, and ultimately violet flakes, which are turned brown by heating, but are decolourised by ammonia FeCl, gives a milky pp, soon becoming violet flakes of (a)dinaphthol (a) Naphthol is a powerful antiseptic, more powerful in this respect than (B). naphthol, although less poisonous (Maximovitch, C R 106, 366)

Reactions -1 On boiling in the air, or on heating in sealed tubes at 350°-400°, it yields dinaphthylene oxide (C10H6),O (Merz a Weith, B 14, 196) -2 Heated to 270° for 8 hours with four times its weight of ammoniacal CaCl, (damp) it yields about 74 pc of (a) naphthyl-If ammoniacal ZnCl, is used instead of CaCl, the product is 60 p c of (aa) dinaphthylamine (Benz, B 16, 14, cf Merz a Weith, B 14, 2844).—3 Aniline and CaCl, yield, on heating, a little phenyl naphthyl-amine (M a W) -4 Ammonium acetate at 270° yields the acetyl derivative of (a)-naphthylamine (Calm, B 15, 615) —5 Ammonium formate at 250° yields CO and (a) naphthylamine —6 When (a) naphthol (2 pts) is heated with anhydrous oxalic acid (1 pt) and cone H_2SO_4 (1 pt) at 130°, there is formed a compound C2.H12O2, crystallising from chloroform in pale rose coloured leaflets, insol alcohol and ether, converted by potash fusion into the acid C₂H₁₄O₃ (crystallising in golden green tables), and yielding the halogen deriva tives C22H10Cl2O and C2H10B12O2, both of which crystallise in the monoclinic system (Honig, M 1 251) -7 Boiling with KClO, and HCl yields di chloro naphthoquinone (Wichelhaus, A 152, 801) —8 Chlorine, acting on (a) naphthol dissolved in HOAc, forms C₁₀H₂Cl₂OH [108°] and $C_6H_4{<}^{\mathrm{CO}}_{\mathrm{CCl}}\stackrel{\mathrm{CCl}_2}{\mathrm{CH}}$ [121°] When the liquid is

kept cold the product is C_eH₄ CO CCl₂ CClH [157°] (Zincke a Kegel, B 21, 1030, 1044) B PCl, at 100° forms di naphthyl phosphate
At 150° it yields (a) chloronaphthalene (Oehler,
B 15, 312) —9 Conc HClAq at 200° yields di naphthyl oxide -10 Aluminium and wodine yield aluminium (a)-naphthol (Gladstone a Tribe, On distillation of this body there C J 41, 16)is formed a dinaphthyl [189°] -11 Iodine and potash yield a dark-violet compound (Messinger a Fortmann, B 22, 2322) -12 Somewhat more readily oxidised by KMnO4 than (B) naphthol (Dreyfus, C = R = 105, 523) —13 H_2SO_4 yields In presence of mono and di-sulphonic acids HOAc it also forms oxy naphthyl methyl ketone 14 HCl, acting on a mixture of (α) naphthol and aldehyde below 0° forms $CH_3 CH(C_{10}H_6 OH)_2$ (Claus a Trainer, B 19, 3004) -15 Di-chloro ether C,H,Cl,OEt yields amorphous C₂₂H,O, or C,H,(O₁₀H₂OH)₃ (Wislicenus, A 243, 165)—16 Benzorc aldehyde yields C₆H₅ CH(C₁₀H₂OH)₂, which turns brown in air (Claisen, B 19, 3316) When boiled with phthalic anhydride it yields naphthol phthalein C₂₈H₁₆O₃ (Grabowski, B 4, 661, 725, 6, 1065) —18 Pyromellitic an hydrids (1 mol), heated with (a)-naphthol (4 mols), at 300° yields the compounds C50H 6O6 and C₅₀H₂₈O, [265°] When the two bodies are heated together in other proportions at 250° there are formed the compounds $C_{40}H_{24}O_{8}$, $C_{40}H_{22}O_{7}$, and $C_{80}H_{18}O_{8}$ (Grabowski) —19 Maleve anhydride and ZnCl₂ at 160° forms $C_{24}H_{18}O_{4}$ and an acid CO₂H CH CH CO C₁, H₂OH [90°] (Burckhardt, B 18, 2868) —20 Benzotrichloride at 100° forms $\{C_0H_3C(C_{10}H_6OH)_2\}_2O$, a reddishbrown powder, insol water, sol alcohol and ether (Doebner, A 257, 58)

Picric acid compound C₁₀H₈OC₆H₂(NO₂)₃OH [190°] Orange needles

(Marchetti, G 12, 503)

Compound with camphor $C_{10}H_{10}OC_{10}H_{10}O$ SG $^{\circ}$ $^{\circ}$ 1 0327 Syrupy liquid, not solid at -16° Not sensibly decomposed by water (Léger, C R 111, 110)

Acetyl derivative C₁₀H, OAc [49°] Formed by heating (a) naphthol with AcCl (Schaeffer, B 2, 131) Formed also by heating a) naphthol with HOAc at 200° (Graebe, A 209, 151), or with Ac₂O and NaOAc (Tassinari, G 10, 471) Large crystals, sol alcohol and ether

Split up into (a) naphthol and acetic acid by distillation with steam On exidation with CrO_s in cold HOAc it yields c exp phthalic acid, and three compounds melting at 114° , 119° , and 121° respectively (Miller, B 14, 1601)

Benzoyl derivative C₁₀H, OBz [56°]. Crystals, v sol ether (Markopar, Z 1869, 216)

Methyl ether C₁₆H, OMe (270°) (V), (258°) (S), (266°) (M), (265°) (H), (269° 1 V) (N a B) S G 12 10974 (S), \(^12\) 10964 (Nasını, G 15, 84) Prepared by the action of McCl on sodium (a) naphthol (Vincent, Bl [2] 40, 106) or of McI (60 g), KOH (25 g), and McOH on (a) naphthol (60 g) (Staedel, A 217, 42) Formed also by heating (a) naphthylamine with methyl alcohol and ZnCl₂ at 200° (Hantzsch, B 13, 1347), and by heating McOH with (a) naphthol and HCl (Manchetti, G 9, 545) Prepared by boiling (a) naphthol for several hours with McOH and ZnCl₂ (Green, priv com) Liquid, smell ing like orange blossom, sol alcohol, ether, and benzene With HNO, it gives a tri-nitro derivative [128°] With pieric acid it forms a compound crystallising in red needles, decomposed by alcohol

Ethyl ether C₁₀H, OEt (281° cor) Formed from (a) naphthol, KOH, and EtI in alco holio solution (Schaeffer, A 152, 286), or from (a) naphthol (25g), MeOH (25g), and H SO₄ (10g) at 125° (Gattermann, A 244, 72) Heavy oil Converted by HNO₃ into a tri intro deriva tive C₁₀H₄(NO₃)₃OEt [148°] (Stredel, B 14, S99)

Propyl ether $C_{10}H_7$ OC_3H_7 (290° cor) $S G = \frac{184}{4} 10447$ (Nasını a Bernheimer, G = 15, 84)

Ethylene ether $(C_{10}H,0) C H_4$ [126°] Plates (from alcohol) (Koelle, B 13, 1956)

(a) Naphthyl ether v Di naphthyl oxide Nitroso derivatives v Oxim of (a) and (β) naphthoquinone

Properties -Plates or tables, sl sol hot water, v sol alcohol, ether, chloroform, and benzene Readily sublimes May be distilled by superheated steam Powerfully antiseptic (Bouchard, Maximovitch, C R 106, 1441) Pine wood dipped in an aqueous solution of (8) naphthol and then in HClAq becomes green on exposure to daylight Bleaching powder colours a solution of (β) -naphthol slightly yellow, but the colour is destroyed by excess of bleaching powder, on adding ammonia and warming, yellowish flakes separate FeCl, colours its solution slightly green, and, after a time, causes deposition of white flakes (of dinaphthol), which become brown on heating Its solution in NaOHAq yields with mercuric chloride a pp $(C_{10}H_{7}O)_{2}HgHgCl_{2}$ 4aq (Pouchet, C R 106, 276). Is may be estimated by adding standard iodine solution to its solution in warm aqueous NaOH (Messinger a Vortmann, B 23, 2754)

Reactions —1 Alkaline potsissium perman ganate oxidises it to o carboxy cunnamic acid CO₂H C₈H, CH CH CO₂H [184°], and an acid C₂₀H₁₂O₄ [281°] which forms the salts BaA'₂7aq and AgA', an ether EtA' [123°] and a dihydride $C_{20}H_{14}O_{4}$ [224°] (Ehrlich a Benedikt, M 9, 527, 10, 115) When (β) naphthol is boiled with P.O., or even by itself in presence of air, it forms di (B) naphthylene oxide -2 The dry distillation of calcium (β) naphthylate $Ca(OC_{10}H_1)_2$ yields di (β) naphthylene oxide, naphthalene, (β) naph thol, and a compound $C_BH_{14}O$ (?) [300°-305°] (Niederhausern, B 15, 1122) —3 Zinc chloride forms, on heating, isodinaphthylene oxide -4 Chloride of sulphur in presence of CS, or benzene forms (HO C10H.) S and (HO C10H.) S. (Tassmari, G 17, 94, Onufrovitch, B 23, 3356) -5 Boiling with sulphur and caustic soda solution forms (HO C₁₀H_a) S₂ [210°] and a compound melting at 170° (Lange, B 21, 260) —6 By heating (8) naphthol (150 g) with aluminium (10 g) as long as hydrogen comes off there is formed a mixture of (β) naphthol and aluminium (β) naphthylate which when distilled yields di (B)naphthyl oxide (Gladstone a Tribe, C J 41, 15) -7 When heated in sealed tubes with am monia, NH,Cl, acetamide, ammonium acetate or ammonium formate, it yields (B) naphthylamine Heated to 270°-280° for 8 hrs with four times its weight of ammoniacal CaCl2 (damp) it yields 80 pc of (β) naphthylamine and 12 pc of $(\beta\beta)$ dinaphthylamine If animoniacal ZnCl is used instead of CaCl, the product is 4 p c of (β) naph thylamine and 82 p c of $(\beta\beta)$ -dinaphthylamine (Benz, B 16, 9) -8 Reacts with nitroso-dimethyl annline forming (β) naphthol violet $C_{18}H_{16}N_{.0}O$ (Meldola, $C_{.J}$ 39, 37), which is converted by heat into 'evanamine,' a blue colouring matter $C_aH_{\nu_b}N_aO$, (Witt, B 23, 2247) —9 Di chloro quinonimide $C_aH_a(NCl)$, forms a red colouring matter HN $C_bH_3 < \frac{N}{O} > C_{10}H_6$ which forms a blue solution in conc H SO₄ (Nietzki a Otto, B 21, 1714) The free base is a yellow pp, v solutional and ether, and is converted by helt into a greenish blue colouring matter, greatly resembling 'cyanamine' (v supra) -10 Nitrogen volude forms 1000 (β) naphthol, a substance melting at 223°, and an amorphous body (Will gerodt, J pr [2] 37, 446)—11 Di chloro di ethyl oxide CH₁Cl CHCl OEt yields C₂H₁₈ClO [174°] crystallising in plates, insol water, sol alcohol and HOAc (Wishcenus, A 243, 169) 12 When chloring is passed into a solution of (B) naphthol in HOAc and the product is treated with an excess of SnCl, there is obtained [1 2]C₁₀H₆Cl OH [71°] (Zincke, B 21, 3284) This chloro-(\$) naphthol when dissolved in HOAc or chloroform and treated with chlorine yields $C_{\bullet}H_{\bullet} < \stackrel{CCl_{2}}{CH} \stackrel{CO}{CH} (Zincke, B 21, 3540)$ (β) naphthol dissolved in HOAc is treated with excess of chlorine there is formed the compound C₆H₄<CCl₂ CO CHCl CHCl crystallising in plates [103°] or needles [102°] and converted by Na2CO3 into ehloro-(8) napthoquinone [172°] (Zincke, B 21, 8550) When chlorine is passed into a well-cooled 10 pc solution of (8)-naphthol, there is

formed $C_eH_4 < \begin{array}{c} CCl_2 & CO \\ CH & CCl \end{array}$ which crystallises from hot alcohol in thick yellow needles [96°] (Z) -13 Chloroform in presence of a small quantity of aqueous NaOH forms on boiling crystalline $C_{22}H_{14}O_2$ or $C_{10}H_6 < C_{10}(OH) > C(OH)$, its anhy dride C22H12O, an aldehyde C10H6(OH) CHO, an alcohol C, H, O, and resins (Rousseau, C R 94, 133, 95, 30, 232) -14 An acetic acid solution of aldehyde slowly reacts in the cold forming the di (β) naphthyl ether of acetic orthaldehyde $CH_3 CH(OC_{10}H_7)$, [201°] (Classen, B 19, 3318) — 15 A few drops of HCl added to a cold solution of benzoic aldehyde and (B) naphthol in HOAc forms C_eH_s CH($OC_{10}H_7$)₂ [205³] converted by heating with HOAc and hydrochloric acid solu tion into O_6H_5 CH $< \frac{C_{10}H_6}{C_{10}H_6} > O$ [190°] (Claisen, B 19, 3316) OB 19, 3316) On adding H.SO, (2 pts) to a solution of benzoic aldehyde (3 pts) and (3) naph thol (6 pts) in alcohol (3 pts) there is formed C, H460 [191° uncor], a crystalline substance, os H₁₆C₁C₁₆H₁, a crystalline statement, not affected by boiling Ac₁O, and converted by fuming HNO₃ into C₄₈H₁,(NO) O (Trzenski, B 17, 499)—16 Benzotrehloride at 100° forms {C,H₂C(O C₁₆H₁) } O which melts above 350° and may be distilled It crystallises in white needles, insol water, alcohol, and ether, sol nitrobenz ene (Doebner, A 257, 59)

Combinations -With picric acid C₁₀H₈O C₆H (NO)₃OH [155°] Orange yellow vater (Marchetti, G 12, 504) —With aniline C₁₀H₂OC₂H_N [82 4°] Crystalline powder (from ligioin) (Dyson, C J 43,409) —With p toluid in e C₁₀H₂OC₂H₂N [80 8°] (D) Acetyl derivative C10H,OAc [70°] (O

Miller, B 14, 1602) Small needles

Benzoul derivative C10H,OBz Nodular groups of needles (Markopar, Z 1869,

Methylether C11H10O ne C10H OMe [720] (Staedel, A 217, 43), [70 5°] (Vincent, Bl [2] 40,106) (274°) (Marchetti, G 9 545) Formed from (3) naphthol, KOH, MeOH, and MeI or Formed also by boiling (B) naphthol with MeOH and ZnCl₂ White plates (from alcohol), insol cold water, v sol ether Volatile with steam With HNO₃ (S G 15) it gives at 0° a tri nitio derivative [213°]

Ethyl ether C10H OFt [33°] (275°). Formed from (8) naphthol, KOH, and EtI (Schaffer, Liebermann, B 15, 1428) Crystalline mass, decomposed in a sealed tube at 310° into ethylene and (3) naphthol (Bamberger, B 19,

Bromo ethyl ether C10H OC1H1Br Prepared by the action of ethylene bromide and KOH on (3) naphthol (Koelle, B 13, 1954) Colourless plates, sol alcohol Alcoholic ammonia at 100° converts it into amorphous C10H, O CH2.CH2NH2, while aniline yields crys-

talline C₁₀H₁O CH₂ CH₂ NHPh [75°] Methylene ether CH₂(OC₁₀H₇)₂ Ethylens ether C₂H₄(OC₁₀H₇)₂ [217°] S. (benzene) 5 Plates (from benzene), insol alcohol and ether

Ethylidene ether v Aldenyde, vol i. 105

Benzylether v BENZYL- NAPHTHYL OXIDE

Naphthylether v DI NAPHTHYL OXIDE Nitroso- derivative v Oxim of (β)-Naph-THOQUINONE

References - AMIDO, AMIDO DI IMIDO-, BROmo, Bromo-nitro-, Chloro, Iodo, Iodo nitro, and Nitro- Naphthols

(a) Naphthol tetrahydride C₁₀H₁O ι e CH_CH_C CH CH Tetrahydro (a) naphthol $[69^{\circ}]$ (265 5°) at 705 mm Obtained by re ducing (a) naphthol in amyl alcoholic solution by sodium Occurs in the distillate obtained in the preparation of the nitrile of the tetrahydride of (a) naphthoic acid (Bamberger a Bordt, B 22, 628, 23, 215) Formed also from the tetra 'nydride of (a) naphthylamine by the diazo re iction (Bamberger a Althausse, B 21, 1892) dilvery white monoclinic tables, smelling like shenol, and turning red in air, sl sol water, v sol alcohol and ether Bleaching powder gives only yellowish flakes in its boiling aqueous solu ion (whereas with (a)-naphthol it gives a deep nolet colour) FeCl₂ gives no colouration Ethylether C₁₀H₁₁OEt (259°) at 705 mm formed by means of EtOH, KOH, and EtI

(β) Naphthol tetrahydride ('aromatic') CH, CH, C CH COH CH, CH, C CH CH ar Tetrahydro (β) naph-[58°] (275°) Formed by the action of nitrous acid on 'aromatic' (B) naphthylamine tetrahydride (Bamberger a Kitschelt, B 23, 884) It is also one of the products of the reduction of (B)-naphthol by sodium (v infra) Flat silvery needles, sl sol water, v sol alcohol and ether Smells like creosote Not etherified by heating with alcohol and H2SO4 at 100° Not affected by heating with cone H_2SO_4 , hot dilute H_2SO_4 appears to form di naphthyl oxide octohydride $(\tilde{\mathbf{C}}_{10}\mathbf{H}_{11})_2\mathbf{O}$ (Bamberger a Lengfeld, B 23, 1129) Bleaching powder added to its aqueous solution lorms a white flocculent pp FeCl₃ gives a bluish green colour, and, on warming, a brownish yellow flocculent pp Chloroform and caustic soda give a greenish yellow colour NaNO₂ added to its solution in conc H₂SO₄ gives a rose red colour Forms a wine red compound with liazobenzene sulphonic acid The sodium salt C₁₀H₁₁ONa crystallises in silky scales

(β Naphthol tetrahydride ('alıcyclio') CH CH C CH, CH OH, ac Tetrahydro-(β) naph-CH CH C CH, CH2 (178° at 53 mm), (264°) at 716 mm Formed by adding sodium to a boiling solution of (3) naphthol in isoamyl alcohol (Bambeiger a Lodter, B 23, 204), and separated from the accompanying 'aromatic' isomeride by aqueous NaOH, in which it is insoluble (Bamberger a Kitschelt, B 23, 885) V sl sol water, v sol alcohol and ether On warming with KOH it yields naphthalene dihydride HI yields an nodide, which readily splits up into HI and naphthalene dihydride Does not react with

diazo compounds

Benzoyl derivative C10H11OBz [63°] (255° at 40 mm) Formed by heating with HOBz at 170° (Bamberger a Lodter, B 23, 209) Tables, v e sol warm alcohol and benzene Split up on distillation into benzoic acid and naphthalene dihydride

Acetyl derivative C₁₆H₁₁OAc (169° at mm.) Formed by the action of HOAc at

140°-150° Decomposed at 268°-280° into HOAc and naphthalene dihvdride

NAPHTHO-LACTONE v Anhydride of Oxy-NAPHTHOIC ACID

NAPHTHOL ALDEHYDE v OXY MAPHTHOIC ALDEHYDE

NAPHTHOL-AZO- compounds v Azo com POUNDS

DINAPHTHOL v DI OXY DINAPHTHYL

(a) NAPHTHOL BLUE C, H, NO NMe₂ C₆H₄.N< O Indophenol Formed by

the action of nitroso dimethylaniline on (a) naphthol, and by the action of dibromo (a) naphthol on dimethyl p phenylene diamine in alkaline solution (Kochlin, Bull de Mulh 52, 532, Witt, S C I 1, 255) Obtained also by oxidising a mixture of di methyl p phenylene diamine and (a) naphthol or (a) naphthylamine with dilute K₂Cr₂O₇ and HCl (Pabst, Bl [2] 38, 161, Möhlau, B 16, 2851, 18, 2913) Bluish violet crystals, with bronze lustre (from alcohol), insol water Dissolves in HClAq with yellow colour, being split up into (a) naphthoquinone and dimethyl p-phenylene diamine

NAPHTHOL CARBOXYLIC ACID v OTY NAPHTHOIC ACID

(a) NAPHTHOL-GLYCURONIC ACID C₁₆H₁₆O₇ [203°] Occurs in urine after taking (a) naphthol (Lesnik a Nencki, B 19, 1537) Long needles, v sl sol chloroform Split up by dilute HClAq into (a) naphthol and glycuronic acid Its aqueous solution is coloured a transi

ent green by H2SO.

(3) Naphthol - glycuronic acid $C_{16}H_{16}O$, [150°] [α] = -88° Occurs in the unine of dogs dosed with (B) naphthol, and can be separated through the insolubility of the lead salt (Lesnik a Nencki, B 19, 1534) Needles (containing 2aq), sl sol water, v sl sol chloroform Conc H,SO, gives an intense green colour Split up by HClAq into (β) naphthol and glycuronic acid -CaA'2 4aq

(a) NAPHTHOL - MALEIN C. H16O. te CH CH C(C₁₀H₆ OH)₂ [118°_120°] together with a compound C14H10O4, by heating (a) naphthol with maleic anhydride and ZnCl. Violet powder, consisting of microscopic four sided tablets Dissolves in alcohol to a red so lution, which on addition of NH, assumes a deep greenish red fluorescence Sol ether, chloro form, and acetic acid, insol benzene and CS. (Burckhardt, B 18, 2867)
NAPHTHOL SULPHIDE v DI - ONY - DI

NAPHTHYL SULPHIDE

(1, 2) - NAPHTHOL SULPHONIC ACID [12] C₁₀H₆(OH)SO₃H (a) - Naphthol 'a' sulphonic acid [101] Prepared by heating (a)maphthol (1 pt) with cone H,SO, (2 pts) on a water bath (Schaffer, A 152, 293, Claus, B 15, 312, Baum, G P B 4197 of June 30, 1883, Monit Scient 1883, 1122) Long, radiating, very deliquescent needles, v sol water and alcohol. Dissolves in HNO, the solution slowly depositing di-nitro (a)-naphthol. FeCl, colours its solution deep blue, changing to green on warming, but becoming blue again on cooling Gives no colour with bleaching powder POl_a (2 mols) at 120° yields chloro-naphthol [57°] and di-chloro naphthalene [94°] (Olaus a. Ochler, B 15, 813)

Salts —CaA'₂3aq Small laminæ, v sol. water —PbA'₂4aq needles, v sol water — PbC₁₀H.SO. (dried at 100°) minute needles

PbC₁₀H_sSO₄ (dried at 100°) minute needles Ethyl derivative C₁₀H_s(OEt) SO₂H Obtained from the acid by treatment with alcoholic KOH and EtI (Maikopar, Z 1870, 306)—
KA'½aq crystalline powder, sl sol cold water

(1, 3?) Naphthol sulphonic acid C₁₀H₈SO₄ is C₁₆H₄(OH) SO₂H (a)-Naphthol' B' sulphonic acid [90° uncor] Formed, together with other sulphonic acids by sulphonation of (a) naphthol in acetic acid solution by means of furning sulphuric acid (80 pc SO₂). It is separated from concomitant products by the sparing solubility of its bailum or lead salt. Deliquescent, long, fine needles. Very unstable, being converted into (a) naphthol and H₂SO₄ by boiling its dilute aqueous or alcoholic solutions. The sodium salt cannot be converted into the chloride by PCl₂, but at once yields di chloro (a) naphthol

C'H CCI [30o]

Salts — NaA' easily soluble white silvery plates — \times KA' easily soluble needles — BaA', aq colourless plates, v sl sol coldwater — PbA', aq small plates, v sl sol coldwater (Baum, Claus a Knyrim, B 18, 2924)

Ethyl derivative C₁₀H₄(OEt)SO₄H [1 3?] Obtained by heating the ethyl ether of (a) naphthol (7 pts) with H₂SO₄(5 pts) at 100° (Mukopar) — KA'aq large glittering plates, sl sol cold water—BaA'. [55°-60°] This acid is perhaps identical with the preceding

(1, 4) Naphthol sulphonic acid

[14]C₁₆H₆(OH)SO₂H [170°] Formed by diazo tising the corresponding (a) naphthylamine sulphonic acid and heating the resulting diazo naphthalene sulphonic acid with dlute H₂SO₄ (Nevile a Winther, C J 37, 632, Monit Scunt 1884, 39, Erdmann, A 247, 341) Plates, vesol water Converted by dilute HNO₃ into dinitro (a) naphthol Chromic acid oxidises it to (a) naphthoquinone FeCl₃ colours its solution greenish blue, but on warming the colour becomes red Its sodium salt is vsol 90 pc alcohol, from which it crystallises in needles

(1, 1') Naphthol sulphonic acid [1 1]C₁₀H₄(OH) SO₂H [107°] Obtained from the corresponding (a) naphthylamine peri sulphonic acid by diazotisation, the product being boiled with water The resulting anhydride (v infra) is heated with alcoholic ammonia for half an hour at 130°, and the ammonium salt thus obtained converted into lead salt, and thence into the free acid (Erdmann, A 247, 346) Deliquescent crystalline mass (containing aq), ve sol water Gives with FeCl₂ a green colour changing to red

shanging to red Salts —NH₄A' v sol water, but not deli-

crystalline powder

Anhydride C₁₀H₅O_{SO₂} Naphthosultone [154°] Formed as above Prisms (from benzene), v sl sol CS_p, sl sol alcohol, v sol chloroform, insol water Boils between 360° and 448° Not attacked by aqueous NH₂₁, Na₂CO₂₁, or cold NaOHAq Boiling NaOHAq converts it into the corresponding and

(1, 4) Waphthol surphonic acid [1 4] $O_{18}H_4$ (OH)SO $_2$ H [110°-120°] Obtained from the corresponding naphthylamine sulphonic acid by diazotising and boiling the product with H_2 SO $_4$ (1 pt) diluted with water (4 pts) (Erdmann, A 247, 343) Hygroscopic crystalline substance

(1, 2') Naphthol sulphonic acid Formed by partial hydrolysis of heteronucleal (α) naphthol disulphonic acid (Liebmann a Studer, E P

7812 [1887]) Yields azo dyes

(a) Naphthol disulphonic acid (Heteronucleal) $C_{10}H_3(OH)(SO_3H)_2$. Obtained, together with the trisulphonic acid, and probably also the (1, 2, 4) disulphonic acid, by heating (a)-naphthol (1 pt) with H_sSO_4 (containing an additional 20 pc of SO_3) (5 pts) for two hours on a water bath (Claus a Mieleke, B 19, 1182) Best prepared by heating (a) naphthol (1 pt) with cone H_sSO_4 (3 to 4 pts) at 130° Yields a nitioso compound $C_{10}H_4(OH)(NO)(SO_3H)_2$ (Seltzer, G P 20,716, Jan 30, 1882) Combines with diazo compounds On nitration it forms di nitro naphthol sulphonic acid

Chlorids C₁₀H₅(OH)(SO₂Cl)₂ Liquid, v sol ether Converted by PCl₅ into trichloro

naphthalene [82°]

Ethyl derivative C₁₀H (OLt)(SO₃H)
Formed by sulphonating the ethyl ether of (α)
naphthol with fuming H₂SO₄ (10 p c additional
SO₃) (G P D 1501, June 7, 1883) Cone HNO₃
converts it into di nitro naphthol sulphonic acid

(a) Naphthol disulphonic acid (Homonucleal) C₁₀H₃(OH)(SO₃H)₂ [1 2 4] Formed by heating (a) naphthol with H₂SO₄ (4 pts) at 70° Differs from the preceding acid in not yielding a nitroeo derivative or forming azo dyes (Schultze, Dissociation, Freiburg, 1883, Bender, B 22, 993) It yields di nitro naphthol on nitiation

(1, 1', 4) (a) Naphthol disulphonic acia [1 1' 4] C₁₀H₃(OH)(SO₂H)₂ (a)-Naphthol (5) sulphonic acid Formed from (a) naphthylamine peri sulphonic acid by sulphonation and diazo tisation Formed also by sulphonating naphtho sultone (Bernthsen, B 23, 3088) Readily forms an anhydride—*Na.A" plates, v sol water FeCl₂ colours its solution deep blue—*BaA"

Anhydride $C_{10}H_3(SO_3H) < {0 \atop SO} > Salts$ NaA' 3aq, m sol water Gives no colour with

FeCl, - *BaA', v sol water

Mono amide C₁₀H (SO₃H)(OH)(SO NH₂) From the anhydride and NH₃ —NaA'2aq Plates

(1, 1', 3) (a) Naphthol disulphonic acid [11' 3] C₁₀H₅(OH)(SO₃H)₂ (a) Naphthol 'ε' disulphonic acid Formed from (a) naphthylamine 'ε' disulphonic acid by the diazo reaction (Bernthsen, B 22, 3330, cf Ewer a Pick, Monit Scient 1889, 604) —Na₂A'' 6aq prisms, v e sol water Its solution is coloured deepblue by FeCl₂

Anhydreds C₁₀H₅(SO₅H)<0 Naplethosultone sulphonic acid Formed by boiling diazonaphthalene 'e'-disulphonic acid with

dilute H₂SO₄ Needles (containing aq)

Mono-amide [1 1' 3]
C,BH,(OH)(SQ,NH,)(SO,H)

Amide sulphonic acid Formed by the action of NH, on the anhydride Needles or prisms, m. sol water—NaA'aq needles, v. sol hot

water -NH, NaA'aq crystals, v e sol water --

BaA', 5aq crystals, m sol water
(a) Naphthol trisulphonic acid C₁₀H₈S₈O₁₀ r e C₁₀H₄(OH)(SO₃H)₂ [1 2 4' 4] Formed by heat ing (a) naphthol with fuming H₂SO₄ (containing 70 pc additional SO₃) at 50° (Seltzer, G P 10,785, Dec 1879, Caro, B 14, 2028, Claus a Mielcke, B 19, 1182) Slender needles Dilute Dilute HNO, at 50° yields di nitro naphthol sulphonic acid It does not yield azo dyes or a nitrosoderivative -K₄C₁₀H₄S₃O₁₀, crystals, v sol water (Lauterbach, B 14, 2028)

Chlorade C₁₀H₄(OH)(SO₂Cl), Plates (from chloroform), sl sol either, decomposed by fusion Converted by PCl, into tetra chloro naphthalene C, H, Cl, [140°] and C, Cl,

(2, 1') - (3) Naphthol sulphonic acid [2 1'] $\mathbf{C}_{10}\mathbf{H}_{6}(\mathbf{OH})(\mathbf{SO}_{3}\mathbf{H})$ (Pfitzinger a Duisbeig, B 22, 396, Armstrong a Wynne, C J Proc 1889, 50) (β)-Naphthol 'a'-sulphonic acid Bayer's acid Rumpff's acid Formed, together with the isomeric acid of Schaffer, by stirring (β) naphthol (1 pt) with cone H.SO. (2 pts) at about 50° (Bayer a Co, G P 18,027, March 18, 1881) When (3) naphthyl sulphate C10H,OSO3H (obtained by the action of H2SO4 on (B) naphthol at a low temperature) is mixed with H2SO4 at 20° it slowly changes to (\(\beta\)) naphthol '\(\alpha\)'sul phonic acid The two isomeric acids of Schaffer and of Bayer may be separated by means of their lead salts (that of the former acid crystallising well) or by treating their sodium salts with 90 p c spirit, which dissolves the salt of Bayer's acid but not that of Schaffer's acid Formed also from (B) naphthylamine 'a' sulphonic acid (Badische) by diazotising and heating with dilute H₂SO₄ (Forsling, B 20, 2102)

Reactions -1 Converted by PCl, into chloro-(8) naphthol [101°] and di chloro naphthalene [61°] - 2 Potash fusion yields di oxy naphthal ene [175°] -3 With diazotised xylidine it yields in concentrated, but not in dilute solutions,

crocem scarlet

Salts -Forms two series of salts-neutral and basic — NaA' glistening six sided plates, v sol water, sl sol alcohol — Na₂C₁₀H₀SO₄ needles, v sol alcohol, v e sol water - ZnA', 2aq needles — $PbA'_2 2^1_2$ aq colourless glistening rhombohedra — $C_{10}H_aSO_5Pb_2$ small yellow crys tals — $C_{10}H_aSO_4(PbOH)_2$ red crystals (Claus a Volz, B 18, 3154)

(2, 3') Naphthol sulphonic acid

[2 3'] $C_{10}H_{\bullet}(OH)(SO_{s}H)$ (B) Naphthol 'B'-sulphonic acid Schäffer's acid [125°]

Formation — 1 By heating (B) naphthol

(1 pt) with cone H₂SO₄ (2 pts) on a water bath (Schaffer, A 152, 296, Armstrong a Graham, C J 39, 135)—2 By fusing naphthalene (8) disulphonic acid with potash (Ebert a Merz, B 9, 610, 10, 592) --3 From (β) naphthylamine sulphonic acid (Brönner's) by the diazo reaction

Properties - Small, non deliquescent laminæ, ▼ sol water and alcohol FeCl, turns its solu tion slightly green and, on warming, brown flakes are deposited Bleaching powder gives a yellow

Reactions -1 Potash-fusion yields di oxynaphthalene [213°] -2 Nitrous acid forms a nitroso-derivative -3 Bromine water gives mono- and di bromo derivatives The K salt

dissolved in HOAc gives with Br yellow plates of C10H4BrSO6K, which form a blood red aqueous solution -4 Cone HClAq at 200°-210° splits it up into (3) naphthol and H_2SO_4 —5 The potas sium salt (1 mol) heated with PCl₃ (2 mols) at 100° forms gelatinous anhydro naphthol sul phonic acid C₁₀H_s(OH) SO₂ O C₁₀H₆ SO₃H, sol water, alcohol, and ether The K salt of this acid crystallises in colourless plates, and is de composed by boiling alkalis with reproduction of (β) naphthol sulphonic acid (Claus a Zim mermann, B 14, 1481) The K salt (1 mol) heated with PCl₃ (2 mols) at 150° forms (SO, H C₁₀H₄ O SO₂ C₁₀H₄), O, an amorphous mass yielding a gelatinous potassium salt K A" (C a Z) The (β) naphthol sulphonic acid heated with PCl, also yields chloro (B) naphthol, and finally \(\epsilon\) di chloro naphthalene [135°], both of which bodies yield chloro phthalic acid [148°] on oxidation (Claus a Dehne, B 15, 319)

Salts -KA'xaq S 2 at 15° - NH'A' 3 at 24° Flat prisms or plates (Meldole, C J 39, 41) —CaA'₂5aq silky lamine, v sol water and alcohol, decomposing at 100° —BaA', 6aq narrow prisms (from boiling saturated solution) -PbA'. 6aq small silvery lamine, v sol water

Ethylderivative C10Hu(OLt) SO, H From the (? impure) acid, KOH, and EtI (Maikopar, Z 1870, 366)—KA' needles, sl sol cold water (β) Naphthol (γ) sulphonic acid

[2 4'] C₁₀H_s(OH)(SO,H) Formed from the cor responding (β) naphthylamine sulphonic acid by the diazo reaction (Reverdin a Nolting, Const de la Naphthaline) Yields di oxy naphthalene [135°] and di chloro naphthalene [48°] (Claus,

J pr [2] 39, 315)
(2, 2') (β) Naphthol sulphonic acid (B) Naphthol '8' sul [2 2'] C₁₀H₆(OH)SO₃H phonic acid Naphthol sulphonic acid F [89°] Formed from (β) naphthylamine 'δ' sulphonic acid by the diazo reaction (Bayer a Duisberg, B 20, 1431) Formed also, together with Schaffer's acid, by heating (3) naphthol (100 g) with H.SO, (70 g) for 2 or 3 hours at 105° (Green, B 22, 723, cf Armstrong, B 15, 22) It is also a product of the fusion of naphthalene 'α' disulphonic acid with NaOH at 250° (Wein beig, B 20, 2907) Needles (containing aq), v sol water and alcohol, insol ether (W) PCl (3 pts) at 165° gives di chloro n'iphthalene [114°], the chief product being a chloro naphthyl phosphate [215°] On fusion with potash it yields C₁₀H₈(OH), [186°] Nitrous yields a nitroso derivative, forming the salt C10H, (NO)(OH)SO2Na 2aq crystallising in golden needles

Salts -NaA'21aq S 8 at 15° Plates --Ka' aq crystals, v sol water -MgA' 5 aq

plates —BaA'₂ prisms, sl sol water
(3) Naphthol sulphonic acid Ethylders vative C10H6(OEt) SO3H Formed by warming the ethyl ether of (3) naphthol with H,SO. (Markopar, Z 1870, 366) —KA' aq needles, sl sol cold water -BaA', needles, v sl sol water

(β) Naphthol sulphonic acid Ethylderivative C10H8(OEt)SO3H Two acids of this formula are obtained by treating the ethyl derivative of (β) naphthol with ClSO₂H (Amphlett a Armstrong, C J Proc 3, 144) The Ba salt of one acid is insol water, that of the other is sol, water One of the acids is doubtless identical with the preceding acid

(2, 1'3') Naphthol disulphonic acid [2 1'3'] C₁H₃(OH)(SO₂H)₂ (\$\beta\) Naphthol '\$\beta\\$ desulphonic acid (\$\beta\) Naphthol-G-disulphonic acid Formed, together with the '\$\beta\\$' isomeride, by heating (β)-naphthol (1 pt) with cone or fuming H_2SO_4 (2 or 3 pts) at 100° – 110° , and separated from its isomeride through the greater solubility

of its Ba salt (Griess, B 13, 1956)

Properties -Glistening needles, v sol water and alcohol With diazo compounds it gives scarlets of a much yellower shade than the (a)acid PCl, (5 mols) at 210° forms di chloro-(β) naphthol [125°] and tri chloro naphthalene [90°], this $C_{10}H_{5}Cl_{10}$, when oxidised with CrO₂, yields a syrupy di chloro phthalic acid and a trichloro naphthoquinone, whence aniline forms C₁₀H₃Cl₂(NPhH)O₂ melting at 228° (Claus a Schmidt, B 19, 3173)

Salts - Na2A" tables or prisms, sol water and dilute alcohol -BaA" 8aq small prisms, v.

sol water

(2,3,3') Naphthol disulphonic acid $[2\ 3\ 3']$ $H_3(OH)(SO_3H)_2$ (3) Naphthol 'a' di sul-C₁₀H₅(OH)(SO₃H)₂ (B) Naphthol R disulphonic acid phonic acid Formed as described above (Griess) White glistening needles, v sol water and alcohol, insol ether Exhibits a bluish green fluores cence in ammoniacal solution When heated in a closed vessel with ammonia it yields a naph thylamine disulphonic acid which, on removal of NH₂, gives rise to naphthalene 'a' disulphonic acid of Ebert and Merz (Pfitzinger a Duisberg, B 22, 398)

Salts - NaA" very small soluble needles -BaA" 6aq needles, sl sol cold water, v sol

hot water, insol alcohol

(β) Naphthol-' δ'-disulphonic acid

 $[2\ 2^{\circ}3]\ C_{10}H,(OH)(SO_3H)_2$ Formed by sulphon ating (2, 2') naphthol sulphonic acid (Weinberg, B 20, 2911) Solutions of its salts exhibit green fluorescence -Na₂A" yellowish powder, v e sol water, sl sol 80 p c alcohol -BaA"2½aq prisms S 56 in boiling water

(β) Naphthol-' γ '-disulphonic acid $H_s(OH)(SO_sH)_2$ Formed by the action of $C_{10}H_3(OH)(SO_3H)_2$ CISO, H on (3) naphthol (Armstrong, B 15, 204)

The Ba salt crystallises in large prisms (B) Naphthol trisulphonic acid

 $C_{10}\dot{H}_4(OH)(SO_3H)_3$ Formed by heating (3) naphthol (1 pt) with H_2SO_4 (2 pts) at 70° – 80° Formed by heating (β) adding H₂SO₄ (2 pts) and heating at 120°, finally adding fuming H_2SO_4 (40 pc additional SO_3) (2 pts) and heating at 150° (Levinstein, B 16, 462) Gives no colour with diazotised xy¹idine

References -AMIDO-, and NITRO-NAPHTHOL

SULPHONIC ACIDS

Vol. III

(B) NAPHTHOL VIOLET C18H16N2O Mel-Formed from nitroso-dimethyl dola's blue anılıne and (3) naphthol Dark flocculent powder, forming a red solution in benzene (Meldola, C J 39, 38)

Hydrochloride B'HCl se.

ClMe, N C, H, C) C10 H, Bronzed needles, resembling KMnO₄ Sol water and alcohol aqueous solution is violet, but turned blue by H.SO. Reduces to a leuco base by taking up H. Converted by heat into a blue colouring matter (Witt, B. 28, 2247)

NAPHTHOL-YELLOW S v DINITRO (a)-NAPH-THOL SULPHONIC ACID

NAPHTHONITRILE v Natrale of NaPHTHOIC ACTD

NAPHTHOPHTHALIC ACID A name for NAPHTHALENE DICARBOXYLIC ACID NAPHTHO-OXY-QUINALDINE v OXY MR-

THYL-NAPHTHOQUINOLINE

NAPHTHOPHENAZINE C, H, N : e

[142°] [142°] (above 360°) Prepared by boiling sulpho benzene azo phenyl-(β) naphthylamine with dilute $\mathbf{H}_{2}\mathrm{SO}_{4}(\widetilde{\mathrm{Witt}}, \widetilde{B}, 20, 574)$ Formed by boiling benzene azo phenyl- (β) naphthyl-amine

N C₆H₅ (?) in acetic acid solution ∙ѝ инс₆н,

with conc HCl, aniline being eliminated (Zincke a. Lawson, B 20, 1169) Formed also by treat ing an alcoholic solution of phenyl (β) naphthyl nitrosamine with HCl (Fischer a Hepp, B 20, 2473), and by distilling with zinc dust oxy naphtho phenazine, which is itself obtained by heating with conc HClAq at 190° the amido naphtho phenazine which results from the action of phenylene o diamine on benzene azo (a) naph thylamine hydrochloride (Fischer a Hepp, B 23, 846) Also got by the action of (3) naphtho quinone (1 mol) on o phenylene diamine (1 mol) in 50 p c acetic acid solution at 0°, and by oxidising a mixture of o phenylene diamine and (β) naphthol with alkaline K₃FeCy₆ (Witt)

Yellowish white prisms, subliming at about 200° in long flat needles or prisms, v sol hot benzene, v sl sol alcohol and ether Conc H₂SO₄ dissolves it, forming a brownish red solu Its salts are dimorphous One sulphate crystallises in scarlet needles, the other in garnet red prisms One nitrate forms orange needles, the other brick red needles One hydro chloride forms long reddish yellow needles, and changes at 150° into the second form SnCl, reduces naphthophenazine to a hydride, crystal

lising in violet needles

a Amido-naphthophenasine CisHiIN, C_eH₄<C(NH₂) CH C N C_eH₄ tained by heating o phenylene diamine (1 mol) benzene azo (a) naphthylamine chloride (1 mol) in alcohol at 160° (F a H) Golden needles (from alcohol), insol water, sl sol ether and cold alcohol Its solutions have a yellowish green fluorescence Its solution in cone HClAq or cone H2SO4 is green -B'HCl -B',H.PtCl. —B'HAuCl.
Acetyl derivative C1.H1.AcN,

Yellow crystalline powder

Amido naphthophenazine

 $C_{10}H_{5}(NH_{2}) N_{2}C_{6}H_{4}$ [191°] Obtained by reducing the nitro compound with alcoholic am 23, 176) monium sulphide (Zaertling, B Brownish-red crystals, sl sol alcohol and ether,
ve sol boiling aniline—B'HCl
Phenylo-chloride of Amido-naphtho-

phenasine C22H16N2Cl t.c.

C, H NPhOL Formed by the action of quinone dichlorimide on phenyl-(B). naphthylamine (Nietzki a. Otto, B 21, 1600). нн

Yields a base which is a bluish-violet pp and a nitrate C₂₂H₁₆N₂NO₃ crystallising in slender needles Yields naphthophenazine on elimination of NH, by the diazo reaction

Reference -- EURHODINES

Nitro-naphthophenasine CieHs(NO2) N2 CeH 4 [222°] Formed by heating nitro (3) naphtho quinone with o phenylene-diamine, HOAc, and NaOAc on the water bath (Z) Greenish yellow prisms, sl sol alcohol and ether Forms a crimson solution in conc H,SO, -B'2H2SO, brown plates

NAPHTHOPHENAZINE CARBOXYLICACID [above 300°] $C_{10}H_9N_2(CO_2H)$ Obtained by heating its nitrile with KOHAq under pressure at 225° (Brunner a Witt, B 20, 2663) Needles m sol water and most solvents Conc H,SO, forms a deep red solution, becoming yellow on

Nutrule C16H9CyN2 [237°] Formed from sodium naphthophenazine sulphonate and KCy Forms a cherry red solution in conc H₂SO₄, becoming yellow on dilution

Naphthophenazine sulphonic acid C₁₆H₉(SO₂H)N₂ [above 290°] Formed by sul phonating naphthophenazine with fuming H.SO. (35 p c) (Brunner a Witt, B 20, 2660) Orange red needles, sol boiling water and alcohol KOH yields yellow flakes of a eurhodol H2SO forms an orange red solution -NaA' 2aq

NAPHTHOPIASELENOL v SELENIUM OR-GANIC COMPOUNDS

NAPHTHOPIAZTHIOLE

[81°]. Formed by heating (aß) naphthylene diamine (2g) dissolved in alcohol, with a conc solution of sodium bisulphite (15 c c) at 190° for 7 hours (Hinsberg, B 23, 1393) Long needles Pleasant odour (from MeOH), m sol water Weak base Somewhat volacile with steam Gives a yellow colour with conc H2SO4 duced by tin and HCl to H2S and naphthylene diamine

NAPHTHOPICRIC ACID, so called, v TRI-NITRO-@ NAPHTHOL

NAPHTHO - QUINALDINE METHYL-NAPHTHO QUINOLINE

(a) NAPHTHOQUINOLINE C,3H,N C'H' CH CH C CH CH Formed by heating a -C NCH

mixture of (a) nitro naphthalene, (a) naphthyl amine, glycerin, and H₂SO₄ (Skraup, M 2, 162, 4, 460) Formed also by distilling its dicarb oxylic acid (Doebner a Peters, B 23, 1235) White prisms (from ether), insol water, sol alcohol, ether, benzene, and dilute acids Smells like naphthylamine On oxidation with chromic acid it yields the quinone C13H,NO2 or

C N CH C.H. CO CO C CH CH, which forms orange crystals, [205°], sol alcohol, benzene, ether, and HClAq, insol water KMnO, oxidises it to phenyl pyridine dicarboxylic acid

Salts - Hydrochloride pale yellow reedles — B'2H_2PtCl_e 2aq. bright-yellow prisms, v sl sol water — B'H_2SO₄ yellowish prisms, v e sol. water — B'H_2SO₄ of needles, al sol cold water — B'H_2(NO₂),OH, minute needles Methylo-sodide B MeI 2aq. Needles.

Octohydrids C15H1,N : 6 Crystals (Bam. berger, B 22, 354)

(β) Naphthoquinoline C, H,N ι e

C'H' CH CH C N CH [94°] (above 860°). -C CH ČH

Formed by heating (β) naphthylamine (28 pts) with nitro-benzene (13 pts), glycerin (50 pts), and cone H₂SO₄ (40 pts) at 150°-160° (Skraup a Cobenzl, M 4,436) The crude product is neutralised with alkali, extracted with ether, and distilled In this reaction (1,2) bromo (3) naphthylamine [63°] may be substituted for (3) naphthylamine, and nitro phenol may be used instead of nitro benzene (Lellmann a Schmidt, B 20, Formed also by heating (1,2) nitro (β) naphthylamine with glycerin and H2SO4 (L a S) Obtained likewise by distilling its carboxylic acids

Properties - Colourless crystals, sl sol water, sol ether, alcohol, benzene, and acids Its alcoholic solution gives a brown colouration with FeCl, and a green colour with cupric acetate

Reactions -1 KMnO, oxidises it to (8). phenyl pyridine dicarboxylic acid

Salts -B'HCl 2aq long needles, v sol water, sl sol alconor— 2 crystalline pp — B₂H₂Cr₂O, short golden fc 148°] Yellow needles obtained by adding a solution of ICl in HClAq to a solution of the base (Dittmar, B 18, 1616) -Picrate [252°]

Methylo-rodide B'MeI 2aq [200°-205°] Light yellow needles, exhibiting a blue fluores cence in aqueous solution

Octohydride C₁₃H₁₇N i e CH₂CH₂ C CH CH C NH CH₂ [60°] Obtained -CCH2CH2 CH, CH, Cby boiling (8) naphtho quinoline with isoamyl alcohol, and sodium (Bamberger, B 22, 354) At the same time there is formed an isomeric C.H. CH, CH, CH NH CH, [91°] -CH CH₂ CH₂

Reference - Oxy , Oxy METHYL , and PHENYL-NAPHTHOQUINOLINE

(B) - NAPHTHOQUINOLINE CARBOXYLIC ACID C14H9NO2 & C6H4 CH CH CN CCO4H [187°] Obtained by oxidising methyl (\$\beta\$) naph thoquinoline with KMnO, and H2SO, (Seitz, B 22, 261) White crystalline powder, insol water, m sol boiling alcohol — NaA' 2½aq Crystals, sl sol cold water — BaA'24aq flocculent pp, becoming crystalline on long boiling, misol

water — CuA', 1 aq crystalline, insol water — B'HCl yellow needles, v sl sol boiling dilute HClAq — B', 2H, PtCl, 2aq yellow needles, v sl sol hot dilute HClAq (a) Naphthoquinoline (Py 1, 3) dicarboxylic

acid C,H, CH CH C C(CO,H) CH C N — C CO,H [278°] Formed by oxidising (a) styryl-(a) naphthoquinoline carboxylic acid with cold aqueous KMnO₄ (Doebner a Peters, B 23, 1284) Groups of greenish yellow needles, insol cold water, al sol hot water, ether, cold alcohol, and dilute HClAq, v sol conc HClAq

Salts —The salts of the alkalis and alkaline earths are v sol water The Pb and Cd salts are white pps —CuA" 2aq dirty green pp, sl sol water —Ag₂A" white flocculent pp

(β) Naphthoqunoline (Py 1, 3) dicarboxylic acid C₆H₄ CH CH CN CCO₂H [288°]

Formed by oxidation of (a) styryl (β) naphthoqunoline carboxylic acid by KMnO₄ (Doebner a Peters, B 23, 1240) Very slender light yellow needles, sl sol ether, cold alcohol, and benzene, v sol HOAc and alkalis—BaA', aq white flocculent pp — Ag A'' powder, sl sol water NAPHTHOQUINOLINE SULPHONIC ACID

C₁₃H₂NSO₂ ve C₄H₃(SO₂H) $\stackrel{C}{\subset}$ CH CH C N CH Obtained from (β) naphthylamine sulphonic acid of Forsling (B 20, 2099) by heating with glycerin, H₂SO₄, and nitrobenzene (Immerheiser, B 22, 404, of Gentil, B 18, 201) Small needles, nearly insol water Very dilute solutions of the acid and its salts fluoresce blue—BaA'₂ 4aq Splendid prisms

(a)-NAPHTHOQUINONE C₁₀H₆O₂ te

C₆H, CO CH (a) Naphthaquinone Mol w 158 [125°]

Formation —1 By exidation of naphthalene by CrO, in HOAc (Groves, C J 26, 209, cf Hermann, A 151, 63) —2 By exidising with chromic acid the following bodies naphthylene p diamine, and its acetyl derivative (Liebermann a Dittler, B 6, 945), (a) naphthylamine and its sulphonic acid (Reverdin a Nolting, B 12, 2305), (a) amido (a) naphthol (Liebermann, A 183, 242), and the acetyl derivative of (a) naphthol (Miller, B 14, 1600)

Preparation—1 Naphthalene (10 g) is dissipped in HOAc (60 g), to this is slowly added a solution of CrO_3 (30 g) in water (20 cc) The mixture is heated at 100° Water (30 g) is added, and the liquid, when cooled to 20°, filtered from naphthalene From the filtrate water precipitates naphthoquinone Recrystallised from light petroleum (Japp a Miller, C J 39, 220, c Groves, C J 26, 209, Plimpton, C J 37, 634, Miller, Bl [2] 43, 125)—2 (a) Naphthol orange (Tropeoline 000 No 1) is reduced to sulphanilic acid and (1 4) amido naphthol, the latter is oxidised and the quinone purified by distillation with steam, the yield is 40 pc —3 By oxidation of (a)-naphthylamine (1 pt) with H.SO₄ (6 pts), water (25 pts), and K_2 Cr O, (2½ pts), in the cold (Monnet, Reverdin, a Nolting, B 12, 2306)

Properties - Yellow triclinic needles, which begin to sublime below 100° Volatile with steam V sl sol water and ligroin, v sol benzene, CS., chloroform, ether, HOAc, conc H2SO, and boiling alcohol Smells like quinone Alkalis form a reddish brown solution. It is not attacked by SO₂ in the cold Reacts in alcoholic solution with primary amines forming compounds represented by C10HeO2NR, which may be considered to be alkyl amido-(a) naphthoquinones or more probably as oxy-(β) naphthoquinone alkylimides Secondary amines act forming compounds represented by C₁₀H₁O₂NRR', but diphenylamine acts only in presence of HCl Tertiary amines do not react in this way Hydro naphthoguinone may be used instead of naphthoquinone, being oxidised by the air Salts of amines may be used instead of amines The compounds crystallise in needles (Plimpton, C J 87, 633)

Reactions -1 Naphthoquinone dissolves in aqueous KOH and Na₂CO₂, and on adding acids This is also got by oxidising a red body is ppd naphthalene with CrO, in acetic acid and neutralising the hot liquid with Na,CO, (A. Guyard, Bl [2] 31, 64, Plimpton, C J 37, 641) It is soluble in benzene and ppd from it by light petroleum as a dark red powder This substance was named carminaphthe by Laurent (Rev Scient 14, 560), who ascribed to it the formula C₁₈H₂O₃—2 Boiling natric acid exidises it to phthalic acid—3 Boiling HIAq and P reduceit to hydronaphthoquinone [176°] Tin and HCl act in like manner —4 When boiled with an aqueous solution of an equivalent of hydronaphthoquinone there is deposited on cooling dark purple crystals of naphthoquinhydrone $C_{20}H_{14}O_4$ It is readily converted by oxidising agents into naphthoquinone and by reducing agents into hydronaphthoquinone -5 Bromins in presence of iodine forms di bromo naphthoquinone [218°] (Miller, Bl [2] 43, 126)—6. Heated with benzoic acid at 160° it forms needles of 'benzoinaphthone' $C_2 H_{12}O_3$? which may be purified by successive boiling with amline, and alcohol (Japp a Miller, C J 39, 221) This body is insoluble in ordinary sol vents and in aqueous NaOH Aqueous KMnO oxidises it to phthalic acid It is not affected by ZnEt, and therefore contains no hydroxyl -Boiling fuming HClAq forms a green amor phous powder, insol water, alcohol, and ether, but partially dissolving in HOAc forming a blue solution (Krapp a Schultz, A 210, 178) -8 Phenyl hydrazine reacts forming benzene azo-(a) naphthol C₁₀H₆(OH) N₂Ph — 9 On adding aqueous ammonia to alcoholic naphthoquinone the liquid becomes brown and, by precipitation by water, a red brown amorphous body is formed, probably Laurent's 'carminaphthe' (Plimpton, C J 37, 641) -10 Yellow ammonium sulphide produces a red powder melting with complete de composition at about 300° (Willgerodt, B 20, 2470)—11 When a solution of methylamine (acetate) is added slowly to a small quantity of naphthoquinone dissolved in alcohol, methylamido naphthoquinone C₁₀H₆O₂NMe [232° uncor], is formed It crystallises from alcohol in red needles, which are reduced by SO, forming a substance crystallising in white needles (Plimpton, C = J = 37,639 = 12 When an alcoholic solution of naphthoquinone is mixed with excess of aqueous dimethylamine the solution neutralused with acetic acid and the liquid allowed to evaporate spontaneously, there is deposited a substance C10H3O2NMe2 which crystallises from alcohol in bright red needles [118°] (Plimpton, C J 37, 642) -13 With ethylamine acetate in alcoholic solution a brown liquid is formed If this is boiled with charcoal, filtered and evapodeposits ethyl amido naphthoquinone rated C₁₀H₆O₂NEt as red needles [140°] It may be sublimed, and is soluble in benzene, hardly so in light petroleum (Plimpton, C J 37, 640) -14 Antline in alcoholic solution forms a red liquid. If this solution is heated to boiling and poured into water, the pp washed with dilute acetic acid and crystallised from alcohol, animal charcoal being used, the product is phenyl-amidonaphthoquinone C_1 , H_2 , O_2 , NPh [191°] (Plimpton, C, J 37, 635). It crystallises in red needles, τ .

sol hot alcohol, benzene, and ether Insol light petroleum It forms a crimson solution in cone H₂SO₄ from which it is ppd unchanged by water It forms a purple solution in alcoholic potash It is not attacked by acetic or benzoic anhydride It is attacked by cone HCl at 170° and by aqueous SO₂ at 125°, and ine being among the products (Plimpton, C J 37, 635, cf Zincke, B 12, 1645, 14, 92) -15 p Bromo aniline forms, in like manner, when heated with (a)-naphthoquinone or oxy (a) naphthoquinone, red needles [266°-269°] (Baltzer, B 14, 1899) -16 m Nitro-[266-269] (Baltzer, B 14, 1899)—16 m Natro-amaline yields $C_{10}H_a(NHC_aH_aNO_a)O_2$ [270°] (B) 17 p Natro analine forms $C_{10}H_a(NHC_aH_aNO)O_2$ melting above 270°, which may be reduced to $C_{10}H_a(NH C_aH_aNH_a)O_2$ [177°] (B)—18 Ethyl analine produces $C_{10}H_a(NPhEt)O_2$ crystallising in violet needles [155°] (Elsbach, B 15, 1810)—19 o Tolundine forms $C_{10}H_a(NHC_aH_a)O_2$ crystal lising in red needles (Elsbach, B 15, 689)—20 m Tolundine forms C H (NHC H)O, crystallising p-Tolundine forms $O_{10}H_3(NHC_1H_1)O_1$ crystallising from alcohol in red needles [200°] and forming a crimson solution in conc H₂SO₄ (Plimpton, C J 87, 688, Elsbach, B 15, 687)—21 Drphenyl amme forms C₁₀H₄(NPh₂)O₂ crystallising from alcohol in needles [164°] (Plimpton)

Out C₂H₄ COO— CH or

CH C(NO) CH Nitroso-(a)-naphthol

Formed, together with a greater quantity of the (β)-oxim of (β)-naphthoquinone, by the action of nitrous acid on (a) naphthol (Fuchs, B 8, 626) Prepared by the action of hydroxylamine hydrochloride on (α)-naphthoquinone (Goldschmidt, B 17, 2064) Yellowish needles, de composing at about 190° V sol alcohol and ether, sl sol CS, and hot benzene volatile with steam Dissolves in alkalis, but is reppd by CO. Does not colour mordants (Kos tanecki, B 22, 1347) Reactions —1 Nitrio Reactions —1 Nitric acid converts it into di nitro (a) naphthol -2. Alcoholic K₃FeCy₅ forms nitro (α) naphthol

— 5 PCl₅ forms 'β' di chloro naphthalene
[68°] — 4 Phenyl cyanate unites, forming

C_{1,4}H₅(OH) NO CO NHPh, which crystallises in yellow prisms [170°] (Goldschmidt a Strauss, B 22, 3106) -5 Boiling with aniline and HOAc yıelds phenyl-(β)-amıdo (a) naphtho quinone amlide C₁₀H₅(NHPh) $\stackrel{Q}{<}_{\rm NPh}$ [187° cor] (Brömme,

B 21, 893) -6 p Toluidine forms, in like manner, p tolyl-amido (a)-naphthoquinone p toluide [183° cor] (B) -7ψ Cumidine forms ψ-cumyl amido (a)-naphthoquinone ψ cumidide [181° cor] —8 Naphthylamine forms (a) naphthyl amido-(a)-naphthoquinone-(a) naphthalide [178° cor] —9 Bromine in HOAc forms dibromo-(a) naphthoquinone oxim $C_{10}H_4Br_2 < V_{NOH}$

[175°] (Brömme, B 21, 391) Methyl ether A'Me [100°] Yellow crystals , v sol alcohol, ether, and benzene, insol water, dissolves in H₂SO₄ with a yellow colour (Ilinski, B 17, 2589)

Di-oxim C₁₀H₄(NOH)₂[14] [207°] Formed by boiling the mono oxim for two days with hydroxylamine and alcohol (Nietzki a Guitermann, B 21, 433) Slender colourless needles, sol. alcohol and ther, decomposed by melting With Ac.O it yields Ci.H.(NOAc), [160°] Tin and HOl reduce it to naphthylene-diamine.

Alkaline KMnO, oxidises it to di-nitroso-naph thalene C₁₀H₆(NO)₂, a yellow powder, exploding at 120°

Di-chloro-di-imide C₁₀H_e(NCl)₂ [187°] Formed from naphthylene p diamine hydrochloride and a cold solution of bleaching powder Yellow (Friedlander a Böckmann, B 22, 591) needles (from alcohol and xylene), smelling strongly like quinone Reconverted by reducing agents to naphthylene-diamine Conc HClAq in HOAc converts it into di chloro (a) naphtho quinone [190°]

Dr-phenyl dr-imide C₁₀H₄(NPh), [187°] Formed by heating benzene azo (a) naphthylamine with aniline at 150° (Fischer a Hepp, A 256, 264) Golden plates, sl sol alcohol

Tetrahydride CH, CH, C CO CH CH, CH, C CO CH Obtained by oxidising (a) naphthylamine tetrahydride with Na₂Cr₂O, and H₂SO₄ (Bamberger a. Lengfeld, B 23, 1131)

(β) Naphthoquinone C_eH₄ < CO CO CO Formation —By exidation of amide- (β) naphthel, which is got by reducing its (a) oxim (nitroso (\$\beta\$) naphthol) (Stenhouse a Groves, \$C \ J \ 32, 47, 33, 415, \$A \ 189, 153, 194, 202, Liebermann a Jacobson, \$A \ 211, 40) The amido (\$\beta\$) naphthol may also be obtained by reducing (β)naphthol orange (v Azo- compounds)

Preparation -Amido-(B) naphthol hydro chloride (1 pt) is dissolved in saturated aqueous SO, and when cold the solution is poured into ferric chloride solution (12 pts, containing 12 pts Fe₂O₃) The quinone is deposited as golden

needles (Groves, C J 45, 298)

Properties - Orange needles (from alcohol) or red needles (from ether) Softons and de composes at 115°-120° Has no smell Is not volatile with steam Dissolves in alkalis, form ing a yellow solution, which absorbs oxygen from the air

Reactions -1 Boiling nitric acid forms phthalic acid—2 SO₂ reduces it to hydro (8) naphthoquinone HIAq acts in like manner (S a G) Tin and HClAq reduce it to 'di naphthyl dihydroquinone' C₂₆H₁₁O₄ crystallising in colourless needles [178°] (Korn, B 17, 3021) 3 Dilute H2SO, forms, on warming, 'di naph thyl diquinhydrone' $C_{20}H_{12}O_4$, a black insoluble powder (S a G) -4 Chlorine passed into its solution in HOAc forms chloro naphthoquinone and the compound C.H. CO CO which crystallises in monoclinic needles (containing 2aq) [112°], and, when anhydrous, melts at 128° (Zincke, B 20, 2892) —5 An alcoholic solution of antline forms the anilide C18H11NO2, probably oxy (a) naphthoquinoneanilide $C_{10}H_{\bullet}(OH) < {}_{NPh}^{O}$ (Liebermann a Jacobson, A 211, 75, Zincke, B. 14, 1494) This substance crystallises in red or yellow needles melting above 240°, insol water, sl. sol alcohol and hot benzene It is split up by boiling soids into aniline and oxy-(a)-naphtho quinone Boiling HOAc converts it into phenylamido-(a)-naphthoquinone With NaOEt and alkyl bromides it gives the compounds C_1 - H_1 (OMe) (NPh) [151°], C_1 - H_1 -EthO₂ [104°], C_1 - H_1 -EthO₃ [100°], and C_1 - H_1 -EthO₅ [104°] (Zincke, B. 15, 279). The so-called disnilide of

(β) naphthoquinone, which is formed by heating : di-bromo (a)-naphthol with aniline, is probably the anilide of phenyl amido (8) naphthoquinone $C_{10}H_{\delta}(NPhH){<}_{\rm NPh}^{\rm V}$ It crystallises in orange red needles [179°] (Meldola, C J 45, 157, cf Zincke, B 15, 481) This body has also been as di-phenyl-di imido-naphthol C₁₀H₃(OH)(NPh)₂ (Griess, B 13, 123) The cor responding di-p toluide [c 175°] and di (8)naphthalide [247°], prepared by the same reaction from di bromo-(a)-naphthol, are probably sonstituted in a similar manner —6 amine forms phenyl ethyl amido (3) naphtho-quinone CieHs(NPhEt)O2? which crystallises in thick red needles [165°], insol NaOHAq, and is resolved by dilute HClAq into ethyl amiline and (β) oxy-(α) naphthoquinone (Elsbach, B 15, 691) -7 o Toluidine forms C₁₇H₁₂NO₂₉ pro bably $C_{10}H_{\bullet}(OH) < \bigvee_{NC_{\bullet}H_{\bullet}}$, which crystallises in red needles, sol NaOHAq It is not affected by HOAc at 150° Boiling dilute HClAq splits it up into o toluidine and (β) oxy (a) naphtho-quinone (Elsbach, B 15, 689) -8 p-Toluidine C₁H₁(OH) $\stackrel{O}{\sim}$ N₀H₁Me, which crystallises in red needles [246°], sol NaOHAq On heating with dilute HClAq at 130° it forms (β) oxy (α) naphthoquinone, and this body is probably an intermediate product in the conversion of (β) naph thoquinone p toluide into (a) naphthoquinone p toluide, which takes place on heating with acetic acid at 150° (Elsbach, B 15, 686) It gives the following ethers -- C1, H12MeNO, [150°], $C_1, H_{12}EtNO_2$ [137°], and $C_1, H_{12}PrNO_2$ [139°] (Zincke a Brauns, B 15, 1969) -9 Boiling with ammonium acetate forms (\$) naphthazine

C_{1e}H_e \(\bigcolon \) NHC,H, [156°] Red plates, with golden lustre, v e sol alcohol Reduced by SnCl₂ to amido naphthol Nitric acid oxidises it to di-nitro-naphthol Bromine forms C₁,H_{1,2}Br₂N₂O [254°] p Tolyl hydrassds C₁,H₁₄N₄O * e

 $C_{10}H_4 < \stackrel{\bigcirc}{N} \stackrel{\longrightarrow}{N} \stackrel{\longrightarrow}{N}$

(a) Oxem C_eH₄ C(NOH) CO (B)-naphthol [109 5°] S (alcohol) 2 4 at 18°. Prepared by adding a concentrated aqueous solution of NaNO, (50 pts) to a boiling solution of (B) naphthol (100 pts) and ZnCl₂ (75 pts.) in spirit (600 pts) After cooling, and standing for some hours, the brown sine salt which separates is washed with alcohol, suspended in water

(1000 pts), and digested for a short time with NaOH (90 pts) After cooling, the sodium salt is filtered off, washed with a little water, and de-composed by cold HCl The yield is 110 p c of the naphthol (Henriques a Ilinski, B 18, 704; of Groves, C J 45, 295, Stenhouse a Groves, C J 32, 47, A 189, 146, Fuchs, B 8, 1026).

Properties—Thin plates or short thick orange prisms V sl sol boiling water, sl sol. ligroin, v e sol ether, benzene, and HOAc Volatile with steam (when pure) Reactions -1 Aqueous ammonia at 100° forms a compound C₁₀H₈N₂O, probably the oxim of naphthoquinonimide C10H6 NH which lises from alcohol in green needles [152°], soluble in alcohol, ether, acids, and alkalis is converted by nitrous acid into an unstable nitrosamine $C_{10}H_6 < \stackrel{N(NO)}{NOH} [244^\circ]$, which forms the salts KC10HeN2O2 and AgC10HeN2O2. Naphthoquinonimide oxim is reduced by ammonium sulphide to a base $C_{10}H_sN_2$ [92°-95°] Naphthoquinonimide oxim forms the salts $KC_{10}H_sN_2$ 0, a red powder, C, H₂N₂OHCl, yellow plates, (C₁₀H₁N₂O)₂H₂PtCl₄ 2aq, orange needles, and C₁₀H₂N₂OHNO₃.—2 Dilute nitric acid forms nitro naphthol -3 Ammonium sulphide reduces it to amido naphthol -4 Chlorine passed into a cold solution of the oxim in chloroform yields C.H. C(NOH) CO crystallising in yellowish red needles (Zincke a Schmunk, A 257, 133) This body takes up more chlorine, forming C,H, C(NOH) CO CCl₂—CHCl which crystallises in white needles [186°], and when treated with potash changes to the dichloro derivative C₆H₄ CC(NOH) CO [166°] -5 Bromine added to its solution in chloroform unites forming C10H, NO, Br. crystallising in colourless needles [131°], which dissolve in alkalis, changing to C'H'CH CB crystallising in yellow _CBr' needles [172°] The last body is also formed by adding bromine to a solution of (3) naphtho quinone (a)-oxim in cold HOAc Bromine added to a hot solution in HOAc forms a bromo naphthoquinone [201°] (Brömme, B 21, 886).-6 Phenyl cyanate forms C1. H. NO CO NHPh, crystallising in felted needles [128°] (Goldschmidt a. Strauss, B 22, 3106) -7 SO₂ or NaHSO₂ acting on its alcoholic solution form amidonaphthol sulphonic acid (Schmidt, J pr [2] 42, 156)—8 Anthre in HOAc forms the same phenyl amido naphthoquinone anilide as it forms with the two other naphthoquinone oxims (Bromme, B 21, 893) Salts—NaA' green pp (from alcoholic solution), sl sol water—KA' lustrous green plates, sol water and alcohol— NH, A' green plates — CoA', brownish-red pp — CoA', purple-red pp, soluble without alteration in alcohol, aniline, phenol, conc H2SO,, and HNO, , it is very stable towards acids, alkalis, oxidising agents, and reducing agents (Ilinski a. Knorr, B 18, 699).—NiA', brownish-yellow pp., sl sol. water and alcohol, easily decomposed by acids (difference from the cobalt salt).—FeA',

black pp., insol. water, v. sol aniline, forming a

dark-brown solution — CuA'2, lustrous brown pp, sol dilute HClAq and 50 p c acetic acid —AgA reddish-brown powder, insol water and alcohol Ag(NH₄)A'₂, slender green needles, insol water and alcohol – AgHA'₂, microcrystalline brown pp, sol alcohol (Ilinski, B 17, 2581, 18, 2728)

Methylether of the (a)-oxim C_eH₄C(NOMe) CO [75°] Long Long yellow needles, v sol alcohol, ether, and benzene, m sol hot water, sl sol cold ligroin Forms a deep-red solution in H2SO, Yields (a) amido (8)-naphthol on reduction with tin and HClAq (Goldschmidt a Schmid, B 18, 571)

Ethyl ether of the (a) oxim C_{ig}H₅O(NOEt) [50°-60°] Needles (from al-

cohol-ligroin) (Ilinski, B 19, 341)

Bensoyi derivative C₁₆H₈O(NOBz) [114°]
(β) - Oxim C₆H₄ < CO C(NOH) (β) Nitroso

(a)-naphthol [148°] (W), [152°] (G) This is the chief product of the action of nitrous acid on (a) naphthol (Fuchs, B 8, 626) It may be separated from the oxim of (a) naphthoquinone (v)supra), which accompanies it by means of their sodium salts (Worms, B 15, 1816) It is also obtained by boiling (3) naphthoquinone with hydroxylamine hydrochloride for half an hour (Goldschmidt, B 17, 215) Yellow needles (from benzene), almost msol cold water, m sol ether, v sol alcohol Somewhat volatile with steam Cone H,SO, forms a deep-red solution decomposed by boiling alcoholic potash

Reactions -1 Bromine acting on its solution in chloroform unites forming a dibromide C₁₀H,NO₂Br., crystallising in grey leaflets [155°] (Brömme, B 21, 390) Bromine acting on its solution in HOAc yields the bromo derivative C10HoBrNO2, separating from alcohol in yellow crystals [175°] (B) -2 Alkaline K_sFeCy_e oxidises it to (β) nitro (α) naphthol -3 Nitric acid forms di nitro (a) naphthol and phthalic acid -4 Phenyl cyanate unites with it, forming

C₁₀H₆ < NO CO NHPh, crystallising from benzene in greenish yellow prisms (containing benzene) [120°] (Goldschmidt a Strauss, B 22, 3106) — 5 Amiline in HOAc forms the same phenylamido naphthoquinone anilide as with the other

two isomeric oxims (Brömme)
Salts—NH₄A' lustrous green needles—
NaA' (dried at 110°) reddish brown powder, insol cone NaOHAq, m sol water and alcohol -KA' lustrous green plates -BaA'2 2aq bronzed plates —PbA'2 dark brown scales, insol water - AgA' brownish-red pp

Methyl ether of the (B) oxim

CH CH CH [98°] From the Ag salt and MeI (Fuchs) Formed also by heating (β) . naphthogumone with the hydrochloride of the methyl ether of hydroxylamine (Goldschmidt a Schmid, B 18, 571, 2224) Yellowish green Schmid, B 18, 571, 2224) Yellowish green needles, v sol alcohol Reduced by tin and HCl to (6) amido (a)-naphthol

Ethylether C, H,O(NOEt) [101°] Flat
greenish yellow needles

Bensoyl derivative C10HeO(NOBz) [162°] Di-oxim C₁₈H₆(NOH)₂ [149°] (G a S), [166°] (B), [181°] (K a M) Formed by warming either the (a) or the (B) oxim in con-

centrated methyl alcoholic solution with hydroxylamine hydrochloride at 100° (Goldschmidt s Schmid, B 17, 2066, Brömme, B 21, 392) Formed also by adding an alkaline solution of hydroxylamine to a cold solution of the (a) oxim in caustic soda (Kehrmann a Messinger, B 23. 2816) Yellow needles, forming a reddish yellow solution in alkalis, and a dark red solution in H2SO. On warming with dilute H2SO. or with alkalıs it is converted into an anhydride Phenyl cyanate also brings about this change (Goldschmidt a Strauss, B 22, 8107) Phenyl hydrazine combines, forming C16H16N4O2, which crystallises from alcohol in tufts of long needles [105°-138°] (Polonovsky, B 21, 182) Stannous chloride reduces it to naphthylene (1, 2) diamine Alkaline K_sFeCy₆ oxidises it to di nitroso naph thalene C₁₀H₁₆(NO)₂, which crystallises in needles [127°], insol water and alkalis, v sol alcohol (Leuckart, B 19, 174, 349) The dioxim colours iron and cobalt solutions brown -KC, H, N, O, brownish red amorphous pp, obtained by adding ether to an alcoholic solution of the dioxim and KOEt (Ilinski, B 19, 342) — $AgC_{10}H_7N_2O_2$ dark red pp, obtained by adding ammoniacal AgNO, to an alcoholic solution of the dioxim

Methyl ether of the dioxin. C_eH₄ C(NOMe) C(NOH) CH CH [159°] Formed by action of hydroxylamine on the methyl ether of the (a) oxim Insol water, sol alkalis

(B) - Methyl ether of the C_eH₄ C(NOH) C(NOMe) Formed dioximFormed from the silver salt of the dioxim and MeI, and also by the action of hydroxylamine on the methyl ether of the (β) oxim Yellow oil, turning brown in air Sol alkalis

 $(\alpha) - Ethyl$ ether of the dioxim C.H. CH CH CH [153°] warming an alcoholic solution of the ethyl ether of the (a) ox.m with hydroxylamine hydrochloride Green needles (from alcohol), insol water -KC₁₂H₁₁N₂O₂ brown needles

Anhydride of the dioxim $C_{10}H_6 \ll_N^{N} > O$ [78°] Formed from the dioxim by the action of AcCl, alkalis, or acids Formed also by heating the (a) or (β) oxim with an alcoholic solution of hydroxylamine hydrochloride at 150° (Goldschmidt, B 17, 216, 801) Long colourless monoclinic needles (from ligroin) Insol alkalıs

Peri Naphthoquinone CieHaO2 1.6.

CH C-C-C CH Occurs in small quantity in CH CH C CH CH the product of the oxidation of di bromo (a) naphthol by fuming nitric acid (Meldola a Hughes, C J 57, 632) Slender, pale yellow needles, no definite melting point observed Blackens and decomposes above 220° Sl sol boiling dilute NaOH Gives an azo compound with phenyl hydrazine Not reduced by cold aqueous SO₂. Zinc-dust and HOAo reduces it to the corresponding dioxynaphthalene, which blackens at 205° and forms a diacetyl derivative melting at 227°.

References. - AMIDO, AMIDO OXY-, BROMO,

BROMO AMIDO, CHLORO, NITRO-, and OXY NAPHTHOQUINONE

NAPHTHOQUINONE-PHENAZINE

 $C_eH_4 < COCN > C_eH_4$ Formed by heating o nitro phenyl amido naphthoquinone with alcoholic ammonium sulphide (Leicester, B 23, 2797) Green plates (from alcohol) Its alco holic solution is brown with green fluorescence

NAPHTHOQUINONE PHENYL-HYDRAZ

IDE v Benzene AZO naphthol

NAPHTHOQUINONE TOLAZINE

C.H. COCNCCH CH Formed by reduction of o nitro tolyl amido (a) naphthoquinone with alcoholic ammonium sulphide (Leicester, B 23, 2797) Steel blue plates with green lustre, forming a green powder Conc H.SO, forms a green solution Its solutions in alcohol or HOAc are greenish yellow with faint moss green fluorescence

NAPHTHOQUINONE TOLYL HYDRAZIDE

Toluene A70 naphthol NAPHTHOQUINOXALINE C, H, N, Le

--Ç N СН C.H. CH CH CN CH [62°] Formed by warming naphthylene (as) diamine with the bisulphite compound of glyoxal in presence of some HOAc (Hinsberg, B 23, 1394) Small colourless needles, v sol alcohol and ether, sl sol hot water Volatile with steam Conc H2SO4 gives a deep red colour, turned yellow by addition of water -The sulphate crystallises well The platinochloride is sl sol water

NAPHTHOQUINOXIM v Oxim of Naphtho-

NAPHTHOSTYRIL v Lactone of peri Amido-NAPHTHOIC ACID

NAPHTHOTOLAZINE v Tolunaphthazine (a) NAPHTHOXINDOLE C,H,NO

C₁₀H₀ NH CO [245°] Formed by the action of mineral acids on the sodium salt of (a) naphthindole sulphonic acid (Hinsberg, B 21, 116) Colourless needles (from alcohol) a nitroso derivative, which on reduction and subsequent oxidation forms (a) naphthisatin

C, H, CH, CO. (β) Naphthoxindole [234°] Formed by the action of mineral acids on (B) naphthindole sulphonic acid (Hinsberg, B 21, 114) Faint greenish needles Sl sol water, v sol alcohol, ether, HOAc Not attacked by mineral acids Conc KOHAq dissolves it without change Baryta water at 150° in sealed tubes yields the Ba salt of a strong acid NaNO. in HOAc solution gives a nitroso- derivative [c 240°], crystallising in yellowish red needles M sol alcohol, ether, HOAc, sl sol water

NAPHTHOXY-ACETIC ACID v Naphthyl

derivative of Glycollic acid, vol 11 p 639

NAPHTHOYL BENZOIC ACID C₁₈H₁₂O₂ t.e.

C_{1e}H, CO C₄H, CO₂H [173 5°] Formed by the action of phthalic anhydride on naphthalene in presence of AlCl, (Ador a Crafts, C R 88, 1355) Small white prisms (from dilute alcohol) Its Ba salt crystallises from alcohol in very hygro scopic needles Conc H2SO4 converts it into naphthanthraquinone $C_{10}H_0 < CO > C_0H_4$ (Elbs, B. 19, 2209)

NAPHTHOYL CYANIDE v Nitrile of Nape THYL-GLYOXYLIC ACID

NAPHTHOYL FORMIC ACID v. NAPHTHYL-GLYOXYLIC ACID

(aa) DINAPHTHYL C₂₀H₁₄ te (C₁₀H₇)₂. Mol. w 254. [154°] (above 360°) V D 8 67 (calc

Formation -1 Together with phthalic acid and other bodies by heating naphthalene with MnO, and dilute H2SO, (Lossen, A 144, 77) -2 By distilling (ββ) dioxy dinaphthyl (1 pt) with zinc dust (12 pis), the yield being 65 p c of the theoretical (Walder, B 15, 2170, Julius, B 19, 2549)—3 By distilling (3) 'dinaphthyl diquin one $C_{29}H_{10}O_4$ with zinc dust (Korn, B 17, 3019) -4 By diazotising di amido dinaphthyl one ' (naphthidine), and boiling the tetra azo dinaphthyl sulphate with alcohol (Nietzki a Groll, B 18, 3256)

Preparation - Naphthalene is boiled with MnO₂ and H₂SO₄ (diluted with more than its own bulk of water) The product is boiled with water, filtered, and the residue extracted with alcohol, the alcohol boiled off (in a current of air), and the residue distilled The fraction coming over above 360° is boiled with light petroleum and animal charcoal, filtered, and allowed to crys tallise (Watson Smith, C J 35, 225) No $\beta\beta$ compound is formed

Properties - Colourless plates (by sublims tion), v sol benzene, CS2, HOAc, and ether, m sol alcohol Its solutions exhibit blue fluorescence (K)

Picric acid compound C₂₀H₁₄2C₆H₂(NO₂)₃OH [145°] Reddish-brown needles

(ab) Dinaphthyl $C_{\infty}H_{14}$ [76°] (S), [80°] V D 8 78 (calc 8 77) Formed, together with a larger quantity of the (\$\beta\$) and a very little of the (aa) isomerides, by passing the vapour of naphthalene, mixed with SbCl, through a red hot tube (Watson Smith, C J 32, 559) Small six sided tables, m sol alcohol, ether, and benzene than the $(\beta\beta)$ isomeride

Picrate C₂₀H₁₄ C₅H (NO₂)₃OH [156°] (Weg scheider, B 23, 3199)

(88) Dinaphthyl C20H14 Isodinaphthyl [187°] (S), [189°] (G a T) VD 873 (calc

Formation.—1 By passing naphthalene through a red hot tube (Watson Smith, C J24, 1184) -2 By passing naphthalene and CCl. through a tube at dull red heat 4C10Hs + CCl 2C₂₀H₁₄+4HCl+C (Watson Smith, C J 35, 229)—3 By passing through a red hot tube, naphthalene with chloroform, (α) bromo naphthalene, SbCl, or SnCl, —4 By heating to reduced (b) brome math thalene. ness (a) bromo naphthalene with naphthalene and soda lime (S) -5 By passing C₁₀H₂ and C₁₀H₁Br through a red hot tube packed with Fe.O. (8) -6 By distilling aluminium (β)-naphthol (Gladstone a Tribe, C J 41, 16) -By dropping isoamyl chloride upon naphthalene (100 g) and AlCl, (25 g) at 120°, pentane being also formed (Roux, Bi [2] 41, 379)

Properties — Plates (from benzene), with the fluorescence Much less sol alcoslight blue fluorescence hol, ether, and benzene than either of its iso merides On oxidation with KMnO, or dilute HNO, at 160° it yields phthalic acid CrO, in

HOAc produces a quinone C20H10O4.

Picric acid compound C₃₀H_{1,2}C₄H₂(NO₂),OH. [184°] (Wegscheider, B. 23, 8200) Orange prisms

(BB)-Dinaphthyl sulphonic acid $C_{20}H_{14}SO_2$ ϵ C₁₀H, C₁₀H₀SO₂H Prepared by heating (ββ)dmaphthyl (15g) with cone H₅SO₄ (3g) for 5 hours at 200° (Watson Smith a Takamatsu, C J 39, 552)—CaA'₂2aq white needles, m. sol. hot water, insol. alcohol, ether, and benzene -BaA', 2aq?

(\$\beta\$) Dinaphthyl disulphonic acid

 $O_{10}H_1(SO_2H)$ $O_{10}H_1(SO_2H)$ Two isomeric acids of this formula are formed by heating $(\beta\beta)$ dinaphthyl (10 g) with cone H₂SO₄ (7 g) at 190° for 5 hours (S a T) One gives an in soluble barrum salt, the other forms BaA"xsq, v sol water, and PbA"xaq, a yellowish white crystalline powder

(ββ) Dinaphthyl tetrasulphonic acid

C₁₆H₃(SO₃H)₂C₁₆H₃(SO₃H)₂ Formed by heating (ββ)-dinaphthyl with an excess of Nordhausen sulphuric acid (S a. T) -Pb,A'v 6aq water, insol alcohol, ether, and benzene

References -DI AMIDO-, DI BROMO-, TETRA-

CHLORO, and NITRO-DINAPHTHYL NAPHTHYL-ACETAMIDINE C12H12N2 16 CH₂ C(NH) NHC₁₀H₇. (a) - Naphthyl - ethenyl amidine Prepared by the action of (a) naphthylamine hydrochloride on acetonitrile at 165° (Bernthsen a Trompetter, B 11, 1758) — B'HCl soluble prisms — B'₂H₂PtCl₈ small yellow tables -B'H2C2O4 small crystals -B'2H2SO4 white orystals -B HNO, oil

D1 (a)-naphthyl-acetamidine C22H18N2 te CH₃ C(NC₁₉H.) NHC₁₀H. Formed from (α)-naphthylamine (6 mols), AcCl (3 mols), and PCl₂ (Hofmann, J 1865, 415) Resinous

 \mathbf{D}_{1} -(β)-naphthyl acetamidine

 $OH_{\bullet} C(NC_{10}H_{\bullet}) NHC_{10}H_{\bullet}$ [168°] Formed by heating (β) naphthylamine (6 mols) with AcCl (3 mols) and PCl₂ (1 mol) at 150° (Maschke, C 1886, 824)

(a)-NAPHTHYL-ACETIC ACID C12H10O2 te C, H, CH, CO, H [131°] Prepared by heating (a)-naphthyl-glyoxylic acid with HI and P (Boessneck, B 16, 641) Long silky needles Sol alcohol, ether, acetic acid, benzene, and hot water, sl sol cold water

Amide C,oH, CH2.CO NH2. [181°] (B), [154°] (W) Formed from the acid (B) and perhaps also by the action of yellow ammonium sulphide on (a) naphthyl methyl ketone (Will gerodt, B 21, 534) Colourless needles, sol benzene, acetic acid, ether, CS2, and hot water

NetreleC₁₀H, CH_2 CN (above 300°). Formed from the amide and P_2O , Oil

DI-NAPHTHYL-ACETYLENE

(above 860°) $[225^{\circ}]$ C₁₀H, C C C₁₀H, tained by distilling exo di chloro di naphthylethylene or exo-tri chloro di naphthyl-ethane (1 pt) with soda-lime (10 pts) (Grobowski, B 11, 301) Long silky needles (from alcohol)

(a) NAPHTHYL-ACRYLIC ACID C12H10O2t e. C₁₀H, CH CH CO H (a) Naphthocinnamic acid [207°] (L), [212°] (B) S 014 Obtained by heating naphthoic aldehyde (2 pts) with sodium acetate (1 pt) and Ac₂O (20 pts) at 170° (Lugli, G 11, 394, Brandis, B 22, 2155) Needles, m. sol. hot water, v sol. alcohol and ether Oxi-dised by KMnO, to naphthoic aldehyde and naphthoic acid Combines with bromine form-

ing $C_{10}H$, OHBr CHBr CO_2H [189°]. HBr at 100° yields $C_{10}H$, CHBr CH_2 CO_2H [216°] — CaA'_2 plates — BaA'_2 needles — CuA'_2 —AgA':

white pp, blackening on exposure
NAPHTHYL-ALLYL-THIO UREA C14H14N2S t.e C₁₀H,NH CS NHC₂H₂. [145°] Formed from (a) naphthylamine and oil of mustard Zinin, A 84, 346, Prager, B 22, 3000) Crystals, insol water, v sol alcohol and ether

Dinaphthyl-allyl \u00fc-thioures v DI NAPHTHYL-

IMIDO THIO CARBAMIC ETHER

(a) NAPHTHYL-AMIDO-ACETIC ACID $C_{12}H_{11}NO_{2}$ is $C_{16}H_{1}$ NH CH₂ $CO_{2}H_{2}$ Naphthylglycocoll [199°] (B a N), [198°] (J), [192°] (M) Formed from (α) naphthylamine, chloro acetic acid, and NaOAc at 100° (Bischoff a Nastvogel, B 22, 1808, Jolles, B 22, 2372, Mauth ner, M 10, 251, Forte, G 19, 361) Needles, insol water, almost insol ether, al sol alcohol, v sol acetone Forms a platinochloride and a nitrosamine The Ca salt distilled with calcium formate gives a product crystallising in colourless plates [163°] -CaA'2 3aq tufts of needles -BaA', 2aq — CuA', small plates — AgA'aq silvery plates

Anhydride (C₁₀H, NH CH₂ CO)₂O Formed by heating the acid at 230°

insol ether, sol alcohol

[126°]

Acetyl derivative [154°] -BaA', 5aq

(β) Naphthyl-amido acetic acid C₁₀H, NH CH₂ CO₂H [135°] Formed by heat ing (β) naphthylamine (2 mols) with a solution of chloro acetic acid (1 mol) at 100° (Jolles, B22, 2372, Bischoff, \vec{B} 23, 2005) Minute crys tals (from water), v sol alcohol, ether, and HOAc Yields a nitrosamine C₁₆H₇ N(NO) CH₂·CO₂H crystallising from MeOH in reddish plates

Salts -The Ag salt decomposes on drying the air (β) Naphthylamine

C₁₀H,NH₂HA' [116°] Needles

(a) NAPHTHYL AMIDO CROTONIC Ethyl ether C₁₀H,NH C(Me) CH CO₂Et [45°] Formed by the action of acetoacetic ether on (a) naphthylamine (Conrad a Limpach, B 21, White silky needles, sol ether and benz Yields on heating to 240° (Py 13) oxymethyl (a)-naphthoquinoline, with elimination of alcohol

(β) Naphthyl-amido-crotonic acid Ethylether C10H,NH C(Me) CH CO2Et [66°] Formed by the action of acetoacetic ether on (β) naph thylamine at 100° (Conrad a Limpach, B 21, 532) Large prisms (from alcohol) Y $(Py \ 1 \ 3)$ Oxy methyl (β)-naphthoquinoline heating to 240°

(B)-NAPHTHYL AMIDO-ETHYL OXIDE $C_{12}H_{13}NO$ is $C_{10}H_7OC_2H_4NH_2$ Formed by the action of alcoholic ammonia on the chloro ethyl ether of (β) naphthol (Koelle, B 13, 1955) - B'HClaq. needles. Amorphous mass B',H,PtCl, needles

(a)-NAPHTHYL-AMIDO-METHYL-MALON-AMIC ACID CH, C(NHC, eH.)(CO₂H)(CONH₁) Ethyl ether A'Et [159°] Formed by dis solving a-cyano-a-(a)-naphthyl-amido-propionic ether (q v) in conc H₂SO₄ (Gerson, B 19, 2969) Long white needles, sl sol cold water, more easily in hot water with a beautiful green fluor. escence, v sol alcohol and ether

(a) - NAPHTHYLAMIDO - (β) - NAPHTHO-QUINONE (a)-naphthylamide C₁₀H₂₀N₂O i.e. C₁₀H₄(NHC₁₀H₇) NO₁₀H₇ [178° cor] Formed from (a) naphthoquinone oxim and (a) naphthylamine (Brömme, B 21, 394) Forms a violet solution in alcohol and a blue solution in conc H₂SO₄ Gives a green colour on heating with H₃SO₄

(β) Naphthyl-amido (β) naphthoquinone (β)-

naphthylamide C₁₀H₃(NHC₁₀H₇) < NC₁₀H₇ (247°] Formed by heating di bromo (a)-naphthel with (β) naphthylamine (Meldola, C J 45, 160) Dull, reddish, fibrous needles Feebly basic Insol alcohol, but dissolves when boiled with alcohol and HCl, forming a violet solution Dissolves in hot toluene or chloroform, giving a reddish brown liquid

DI-(a) NAPHTHYL DI AMIDO-OIAZTHIOLE $\mathbf{C}_{22}\mathbf{H}_{16}\mathbf{N}_{4}\mathbf{S}$ i e $\mathbf{S} < \mathbf{C}(\mathbf{NHC}_{10}\mathbf{H}_{1})$ $\mathbf{N} > \mathbf{N}$ [136°] Obtained by oxidising (a) naphthyl thio urea with hydrogen peroxide and dilute HClAq (Hector, B 23, 359) Crystallises from alcohol in white needles containing HOEt (1 mol) and melting at 104° Insol water Cyanogen, passed into its warm solution, forms $\mathbf{C}_{22}\mathbf{H}_{16}\mathbf{N}_{16}\mathbf{C}_{4}\mathbf{N}_{4}$ [223°] Salts — B',H PtCl₈ [225°] — Picrate

Salts — B',H.PtCl₅ [225°] — Picrate B'C₆H.(NO₂)₃OH LtOH [below 100°] Small yellow grains — B'AgNO₃ Pp , insol alcohol Acetyl derivative C₇H₁₃AcN₄S [203°]

Needles (from alcohol)

Benzoyl derivative C₂H₁,BzN₄S [270°]. Di (β) naphthyl di-amido oiazthiole

Acetyl derivative C22H15AcN [203°]

Needles (from alcohol)

Benzoyl derivative C.₂H₁,BzN₄S [247°]
(β) NAPHTHYL PHENYL-AMIDO ETHYL

OXIDE C₁₈H₁,NO te C₁₆H O C.H., NHC.H.,

[75°] Formed by the action of annine on the chloro ethyl ether of (β) naphthol (Koelle, B 13, 1955)

TRI (β) VAPHTHYL - TRI AMIDO TRI-PHENYL CARBINOL (C₁₀H, NH C₂H₄), C OH Formed by heating para rosaniline with (β) naphthylamine (Meldola, C N 47, 133, 147) Dyes wool or silk blue

TRI - NAPHTHYL - TRI - AMIDO - TRI - PHENYL CARBINYL CHLORIDE C₄, H₃₆N₄Cl • ¢ (C₁₀H, NH C₈H₄).C C₆H₄NHCl C₁₀H₇ Phonyl-

(a) naphthyl amine blue. Formed by heating phenyl (a) naphthylamine with oxalic acid (Hausdorfer, B 23, 1965)
v sol hot aniline, sl sol cold alcohol, insol ether and benzene

waphthyl.amido-isosuccinamic acid

Naphthyl.amido-metryl-malonamic acid

(a)-naphthylamine C₁₀H₁N + s

C_eH₄ C(NH₂) OH Naphthaldme Naphthalamme Mol w 148 [50°]. (300°) V.D (at

194°) 72 6 (calc 71 5) (Eykman, B 22, 2757) S. 167 in the cold (Ballo, B 3, 675)

Formation—1 By reduction of nitro-naphthalene by alcoholic ammonium sulphide (Zinin, J pr 27, 143), by iron and acetic acid (Béchamp, A Ch [3] 42, 186, Schutzenberger a Willm, C R 47, 82, Ballo, B 3, 288, 673), or by tin or zinc and HClaq (Böttger, D P J 173, 480)—2 By heating (a) naphthol with four times its weight of ammoniacal CaCl, to 270° for 8 hours,

the yield being 74 p c (Benz, B 16, 14, cf Calin, B 15, 616)

Preparation —Granulated nitronaphthalene (600 kilos) is slowly added to a warm mixture of iron borings (800 kilos), hydrochloric acid (40 kilos), and some water The mixture is agitated and kept at about 50° by blowing in steam for 7 hours, after which milk of lime (containing 50 kilos of CaO) is added The mixture is distilled in a current of superheated steam

(Witt, Chem Industrie, 10, 215)

Properties - White silky needles, with powerful odour May be sublimed V e sol alcohol Colours pine wood yellow and ether not quite pure it rapidly becomes coloured in the Does not turn red litmus blue Aqueous solutions of its salts give a blue pp with FeCl, AgNO, auric chloride, platinic chloride, SnCl, HgCl₂, chromic acid, H O₂, and other oxidising agents (Pina, A Ch [3] 31, 217, 78, 64, Schiff, A 101, 92, Wurster, B 22, 1910) This blue pp , 'oxynaphthylamine' C, H, NO, is amorphous, v sol chloroform, and not reduced by SO, (Schiff, A 129, 255) If to a solution of (a) naphthylamine in alcohol or HOAc there be added a small quantity of nitrous acid and a little HClAq an intense purple colour is produced (Liebermann, A 183, 265)

Reactions -1 Heated with ZnCl2 or CaCl, at 280° it splits up to some extent into NH, and dinaphthylamine -2 Distillation over PbO yields naphthazine -3 Boiling chromic acid mixture oxidises it to naphthoquinone, phthalic acid, and other products (Reverdin a Nölting, B 12, 2306) —4 Heated with nitro naphthalens and some HClAq at 200° it yields 'tri naphthylene diamine' C₃₀H₁₈N₂ (Salzmann a Wichelhaus, B = 9, 1107) -5 Urea (1 pt) heated with (a)naphthylamine (2 pts) at 120° forms only naphthyl urea, but both mono and di naphthylurea are formed on heating (a) naphthylamine hydrochloride with urea at 160° (Pagliani, G 9, 28) -6 Cyanic acid forms (a) naphthyl urea alkyl thro-carbimides form alkyl naphthylthio ureas -8 Alcoholic CS, forms di naphthylthio ures -9 MeOH and ZnCl₂ at 190° form the methyl ether of (a) naphthol (Hantzsch, B 13, 1347) - 10 (a) naphthylamine hydrochloride heated with o amido-azo-compounds yields azine colouring matters (eurhodines) -11 Řeadily converted into naphthalene by diazotising, and pouring the alkaline solution of the diazo- compound into a solution of SnCl, in aqueous NaOH (Fried länder, B 22, 587) -12 SiF, in benzene solution forms minute crystals of Si(NHC10H7)4 (Reynolds, C J 55, 482) -13 The bisulphite warmed with benzoic aldehyde forms CoH, CH NC10H,, a yellow powder (Papasogli, A 171, 188) -14 Bensonc aldehyde and pyruvic acid form the compound $C_{lo}H_{o} < \stackrel{N\cdot OPh}{C(CO_{2}H)} > CH$ crystallising in yellow

needles [300°] (Doebner a Kuntze, A 249, 109) 15 Bensil reacts on heating, forming the compounds C₄H, C(NC₁H,) CO C₄H, [139°] and C₅H, C(NC₁H,) C₄H, [219°] both crystallising in yellow needles (Bandrovsky, M, 9, 685)—16 A cone boiling aqueous solution of alloxan forms a compound C14H11N2O4, which separates in transparent white needles, insol water, and coloured green by H2SO4 Alkalis convert it into a crystalline acid C_{1,}H₁₀N₂O₅ (Pellizari, G 17, 409) —17 Cyanuruc chloride forms N₃C₃Cl₂(NHC₁₀H₇) [149°], N₄C₅Cl(NHC₁₀H₇)₂ [215°], or N₃C₅(NHC₁₀H₇)₃ [223°], according to the proportions used (Fries, B. 19, 242, C J 49, 314)—18 Citraconic acid 25. 13, 222, 0 23, 127, 126 Circlett atta at 145° forms C₁₀H,N C₃H₁O₂ [143°] (360°) (Morawski a Glaser, M 9, 284) —19 Itaconic acid heated with (a) naphthylamine in aqueous solution forms C₁₀H₇N CH₂ CH₂ CO₂H, a white crystalline powder [206°], m sol hot alcohol (Scharfenberger, A 254, 151) -20 Chloro acetic ether in ethereal solution forms C16H16NO2Cl, crystallising in prisms [75°] (Bender, B 20,

2750) Salts -B'HCl Needles (by sublimation) or scales (from alcohol), v e sol water, alco br scales (from alcohol), V sol water, alcohol, and ether $-B'_2H_1PCl_b$ yellow pp, sl sol water $-B'_1H_1PCl_b$ yellow pp, sl sol water $-B'_1H_1PCl_b$ yellow pp, sl sol water $-B'_1H_1PCl_b$ yellow pp, sl sol swater $-B'_2H_1PCl_b$ yellow pp, sl sol swater and specific properties of the state of the distillation C₂O₂(NHC₁₀H₇)₂ and the formyl derivative CHO NHC₁₀H₇ (Zinin, A 108, 228) — B',H,PtCy, crystals (Scholtz, M 1, 905) — B'H₂SO₃ pearly rosettes — Citraconate [99°] Formed by mixing solutions of (a) naphthylamine and citraconic acid in benzene (Morawski a Glaser, M 9, 285) -Phenate B'C₆H₅OH [30 1°] Formed by heating phenol with (a) naphthylamine (Dyson, C = J = 43, 468) Needles (from light petroleum) —Benzene sul-phonate [225°] (Norton a Westenhof, Am 10, 129) — Toluene p-sulphonate [239°] (Norton a Otten, Am = 10, 140)

Formyl derivative $C_{10}H_1NH(COH)$ 9°] White silky needles (Tobias, B 15, [189°]

Acetyl derivative ConH,NHAc

Formed from the base by treatment with AcCl, Ac.O, or HOAc (Rother, B 4, 850, Tomması, C R 76, 1267, Liebermann, A 183, 229) Formed also by heating (a) naphthol with ammonium acetate White silky needles, sl sol boiling water, v sol alcohol On heating with sulphur the products are ethenyl amido-naphthyl mercaptan and $C_{10}H_{\bullet} < N > C C < N > C_{10}H_{\bullet}$, which crystallises in yellow plates [above 300°] (Hofmann, B 20, 1801) The only products of the nitration of acetyl-(a)-naphthylamine are the o- and p-nitro-derivatives of melting points [199°] and [190°] respectively, the supposed isomeride of melting-point [170°] is a molecular compound of the o- and p- bodies, and the so called '\$- and &-nitracetnaphthalides' are diacetyl derivatives of the same two nitro-(a) naphthylamines (Lellmann a Remy, B 19, 796) Chlorine passed into its solution in HOAc forms CheH,Cl,NHAo [214°] (Cleve, B 20, 448)
Chloro-acetyl derivative C,H,cNClO

i.e. C, H,NH COCH,OL. [121°]. Formed from

naphthylamine and chloro acetyl chloride (Tom ması, Bl [2] 20, 21, Abenius, J pr [2] 40, 437) Silky needles

Throacetyl derivative C, H NH CS CH, [96°] (B a T), [111°] (J) Formed by heating (a) naphthyl acetamidine with CS, for several hours at 100° (Bernthsen a Trompetter, B 11, 1760) Formed also by heating acetyl (a) naphthylamine with P₂S₃ (Jacobsen, B 20, 1897) White tables Gives C₁₀H,NH CH₂ CH₃ on re Oxidised by K₃FeCy, to ethenyl duction amido naphthyl mercaptan $C_{10}H_0 < N > C OH_3$

Bensoyl derivative C, H, NHBz [156°] (W), [162°] (Kühn, B 18, 1477), [160°] (Hofmann, B 20, 1798) Colourless needles, v sol dilute alcohol, sl sol absolute alcohol and water (Ebell, B 7, 1317, 8, 562, Worms, B 15, 1814) Yields on nitration $C_{10}H_*(NO_*)NHBz$ [224°] PCl₃ converts it into $C_{10}H_*N$ CClC₄H₃. $[224^{\circ}]$ [60°] (Just, B 19, 984)
Thiobenzoyl derivative

C₁₀H₇NH CS C₆H₅ [148°] Formed from the benzoyl derivative by heating with P2S, , or from (a) naphthyl acetamidine by heating with CS, (B a T , J) Yellowish needles or plates. Oxidised by K₃FeCy₆ to benzenyl amido naphthyl mercaptan

(a) Naphthylamine ar-tetrahydride

C₁₀H₁₁NH₂ ve CH₂CH₂C C(NH₂) CH (275°) at 712 mm S G ¹² 1 0625 Formed by the action of sodium on a solution of (a) naphthylamine in isoamyl alcohol (Bamberger, B 20, 2916, 21, 1789) Thick colourless oil, sl sol water, v sol alcohol and ether, insol NaOHAq Less basic than the (β)-isomeride Reduces Ag from hot solutions, but does not reduce Fehling's solution Readily diazotised Aqueous NaNO, (1 mol) acting on its hydrochloride (1 mol) at 0° forms C₁₀H₁₁ N₂ C₁₀H₁₀NH, (Bamberger a. Lengfeld, B 23, 1134) Yields dyes with diazocompounds KMnO, oxidises it to adipic acid

Salts -B'HCl dimetric plates, v sol water and alcohol -B'HClHgCl, flat white plates, sl. sol cold, v sol hot water -B'2H2SO, laq -Picrate yellow needles

Acetyl derivative C10H11NHAC [158°]. Needles, v sol ether, chloroform, and alcohol (a)-Naphthylamine ac tetrahydride

 $C_6H_4 < \frac{CH(NH_2)}{CH_2} \frac{CH_2}{CH_2}$ (246 5°) at 714 mm. Formed by adding a 10 pc solution of CuSO. slowly at 100° to a solution of amido naphthylhydrazine tetrahydride derived from (1,4') naphthylene diamine (Bamberger a Bammann. B 22, 963) Liquid, sol cold water, v sol hot water, alcohol, and ether Unlike its 'aromatic' isomeride it turns red litmus blue It cannot be Does not yield dyes with diazodiazotised compounds FeCl, has no effect in the cold, but on warming produces a reddish-brown colour K₂Cr₂O₂ and H₂SO₂ give no colour. KMnO₄ oxidises it, in cold dilute solution, to o carboxy β phenyl-propionic acid [166°] — B'HCl needles, v e. sol water — B'₂H₂PtCl₂2a₄. [190°] Orange prisms, sol water -B'HNO. 1890 Needles, v e sol water -B'H2CO needles -Picrate needles, sol hot water.

Acetyl derivative CieHi NHAs. [149].

Prisms or needles, sl sol cold water

(8) Naphthylamine C, H,N t.s

 $C_{e}H$ < $< CH C NH_{2} (294^{\circ})$ (Liebermann

a. Jacobson, A 211, 41)

Formation -1 From the acetyl derivative of (a) naphthylamine by successive bromination, nitration, elimination of Ac, removal of NH2 by the diazo reaction, and reduction of the result ing brome nitre naphthalene by tin and HClAq (Liebermann a Scheiding, A 183, 258) -2 By with heating (β)-naphthol ammonia zinc chloride at 200°, di (8) naphthylamine being also formed (Merz a Weith, B 13, 1300) -3 By passing dry ammonia over strongly heated (β)-naphthol (Graebe, B 13, 1850) —4 By heating (8) naphthol with four times its weight of am moniacal CaCl₂ (prepared by passing NH₃ over ordinary granulated CaCl, containing about 18 p c of H₂O) for 8 hours at 270°-280°, the yield being 80 p c on the naphthol, together with 12 p c of $(\beta\beta)$ dinaphthylamine (Benz, B 16, 8) — 5 In small quantity, together with a large quantity of dinaphthylamine, by heating (B)-naphthol with ammoniscal $\operatorname{ZnCl}_2(B)$

Preparation -1 By passing NH, under pres sure into (β) naphthol at 150°-160° -2 By

heating (B) naphthol (10 pts) with NaOH (4 pts) and NH₄Cl (4 pts) (G P 14,612 [1880])

Properties — White plates (from water) with out odour Volatile with steam Gives no colouration with FeCl, chromic acid, or bleaching powder Its alcoholic solution is not coloured

naphthalene (Volodkevitch, Bl [2] 45, 178) -2

by nitious acid and HCl Reactions -1 Heated with PbO it gives azo

SiCl, forms SiCl₂(NHC₁₀H₇)₂ (Horden, C J 51, 40) A benzene solution of SiCl₄ forms $Si(NHC_{10}H_7)_4$ (Reynolds, CJ 55, 481) —3 With paraldehyde, acetone, and HCl it gives dimethyl- (β) naphthoquinoline (Reed, J pr [2] 35, 298) —
 With methylal, accione, and HCl it forms me thyl (β) -naphthoquinoline, (β) naphthoacridine and a base, $C_{14}H_{20}N_{2}$, which is probably methyl amido naphthyl naphthoquinoline dihydride C₁₀H_e CMe CH NH CH C₁₀H_eNH₂ This base [203° uncor] forms the following derivatives B"C₂H..(NO₂)₂OH — B"Et I₂ — C₄H₂₀N₄O₃ [c 238°] (R) —5 Cyanuric chloride forms O₃N₃Cl₂(NHC₁₀H₂) [154°], C₃N₃Cl(NHC₁₀H₂)₂ 278°], and $C_{2}N_{3}(NHC_{10}H_{7})_{3}$ [209°] (Fries, B 216], and C₂N₃(NHC₁₀H_{1/3} [203] (Fries, B 19, 2056) — 6 Benzouc aldehyde in hot aucoholic solution forms C₄H₃CH NC₁₀H, [103°] which may be reduced by sodium amalgam to C₆H₃CH₂ NHC₁₀H, [68°] which forms a nitros amine C₄H₃CH₂ N(NO)C₁₀H, [112°] (Clausen, A 237, 272, Kohler, A 241, 360) — 7 Benzil at 215° forms C₄H₃ CH(OH) C(NC₁₀H₄) C₄H₃ crystallight of the control of th lising from alcohol in yellow prisms [130°] (Voigt, J pr [2] 34, 22) —8 The compound of glyoxal with KHSO, yields C₁₂H_sNSO₃K crystallising in white plates (Hinsberg, B 21, 110)—9 Malic acid reacts on heating, forming the compounds C₂H₁O(CO NHC₁₀H₁)₂ [263°] and C₁₆H,N CO CH OH [198°] (Bischoff, B 23, 2046) -10 Pyruvic acid and bensoic aldehyde form CPh CH CCO,H (Doebner, A. 249, 109)

11. Quinone chlorimide acts on an alcoholic

 $C_{10}H_{4} < N > C_{6}H_{2}NH_{2}$ (Nietzki a Otto, B 21, 1598) -12 Chloro-acetic acid forms

 $C_{10}H$, NH CH₂ CO NHC₁₀H, [170°] (Cosiner, B 14, 60)

Salts -B'HCl colourless plates, v e sol water and alcohol, sl sol HClAq -B'2H2PtCl yellow plates, sol water —B'₂H₂SO₄ plates, m sol cold water —B'HNO₄ colourless plates, sl sol cold water —Picrate [195°] Long yellow needles, v sol alcohol —Citrate B'C₈H₀O, [89°] (Hecht, B 19, 2616)—Citrate B'C₈H₀O, [89°] Yellow needles (from acetone) (Moraw skı a Glaser, M 9, 285)

Compounds with metallic salts B'2CuSO4 (Lachovitch, M 9, 516) Forms also a compound with mercuric chloride

Formyl derivative C₁₀H, NH CHO [120°] (C, Tobias, B 15, 2447) [129°] (L a J) Formed by heating (β) naphthylamine with formic ether and alcohol (Cosiner, B 14, 58), or with formic acid (Liebermann a Jacobson, A 211, 42) Small plates, sl sol hot water

Acetyl derivative C₁₆H, NHAc [132°] Long needles or plates, sol hot water (Merz a Weith, B 13, 1300, 14, 2343) On heating with sulphur it yields $C_{10}H_{e} < \stackrel{N}{S} > C C < \stackrel{N}{S} > C_{1e}H_{e}$ crystallising in yellow plates, insol most solvents sol nitrobenzene (Hofmann, B 20, 1804) Bromine in HOAc forms C₁H₂Br NHAc [140°] (Lellmann a Schmidt, B 20, 3154)

Thio acetyl derivative C12H11NS ie C₁₀H, NH CSCH, [146°] Formed by heating the acetyl derivative with P₂S₃ (Jacobson, B 21, Needles or plates (from alcohol) dised by K.FeCy, to ethenyl amido naphthyl

mercaptan $C_{10}H_{0} < N \le CMe$ [81°]

Valeryl derivative C,oH, NH COC,H, [138 5°] (Bamberger a Muller, B 21, 1112)

Benzoyl derivative C₁₀H,NHBz [148°] (Cosiner, B 14, 58), [157°] (Hofmann, B 20, 1803) Minute needles, sol ether, benzene, and hot alcohol PCl, converts it into the compound C₁₀H,N CClC₆H₃ [68°] (Just, B 19, 983)

(β) Naphthylamine ar-tetrahydride CieHisN CH_CH_C CCH CNH₂ [38°] (276°)at713mm ČH, CH, C CH CH Formed to the extent of 3 or 4 pc in the prepa ration of the alicyclic isomeride by reduction of (8) naphthylamine (Bamberger a Kitschelt, B 23, 882) Neutral in reaction Its salts are acid in reaction May be diazotised Yields adipio acid on oxidation

(B) Naphthylamine ac tetrahydride

C.H. CHNH, (162°) at 36 mm, (249 5 cor) at 710 mm S G 15 1 031 Formed by reducing (8) naphthylamine with sodium and ısoamyl alcohol (Bamberger a Muller, 20, 2916, B 21, 850, 1115, Bamberger a Kitschelt, B 23, 877) Purified by dissolving in ligroin and pps by CO₂. The carbonate is then dissolved in Colourless Purified by dissolving in ligroin and ppg acetic acid, which leaves a brown oil Colourless liquid, smelling like piperidine, sl sol cold, m sol hot water, v sol alcohol and ether Powerful base with alkaline reaction, displacing ammonia from its salts Absorbs CO2 from the air Possesses no reducing power Carbon disulsolution forming a eurhodine of the formula phide at 0° forms tetrahydronaphthyl ammo

tetrahydronaphthyl thio carbamate nıum C₁₀H₁₁NH₃ S CS NHC₁₀H₁₁ [142°] Phenyl cyanate forms PhNH.CO NHC₁₀H₁₁ [166 5°] Does not yield colouring matters with diazo- compounds Powerful midriatic poison oxidises it to o-carboxy phenyl-propionic acid and phthalic acid Benzoic aldehyde forms C.H. CH NC16H11 [52°] HBrAq at 150° forms naphthalene

Salts -B', H, CO, and B'H, CO, are white crystalline pps, giving off CO₂ in the air—B'HCl [237°] Plates, v e sol water and Blohol B',H_PtCl₆ — B'HAuCl₄ — B'HClHgCl₂
(?) [241°] Prisms, sol hot water — B',H_SO₄ —
B',H_2Cr,O, — B'HNO₈ [212°] White satiny tables, sl sol cold water, v sol cone HNO₂ At 220° it dissociates with explosive violence -B'HNO, [c 160°] Needles (from water), v e sol water, insol ether Not decomposed by boiling water —B'HOAc [156°] Thick mono clinic crystals, v sol alcohol, sl sol ether

Acetyl derivative C10H11NHAc [107°] Prisms, v e sol chloroform and benzene, v sol hot water, m sol ether, insol petroleum ether

Not attacked by bromine in the cold

Benzoyl derivative CieH, NHBz [151°] Needles, v sl sol water, v sol benzene

at 15 mm

Formation -1 By heating (a)-naphthylamine hydrochloride with (a) naphthylamine (Girard a Vogt, Bl [2] 19, 68) —2 A product in the pre paration of methyl (a)-naphthylamine from (a)-naphthylamine and MeCl (Landshoff, B 11, 638) -8 By heating (a)-naphthol with four times its weight of ammoniacal ZnCl, to 260°, the yield being about 60 p c (Benz, B 16, 15)— 4 By heating a mixture of (a)-naphthylamine, (a)-naphthol, and CaCl, to 260°, the yield being 22 pc (B) -5 In small quantities by heating (a)-naphthylamine with CaCl2 or ZnCl2

Properties - Dimetric leaflets (from alcohol), m sol alcohol, v e sol ether FeCl, gives a

green pp in its alcoholic solution

Picric acid compound NH(C₁₀H₇)₂2C₆H₂(NO₂)₃OH [169°] Small glis-

tening black needles

Acetyl derivative NAc(C10H7)2 Nitrosamine (C10H7)2N NO [262°] Formed by adding rather more than the theoretical quantity of powdered NaNO, to a solution of di-naphthylamine in HOAc (L , Wacker, A 243, 800) Yellow crystalline powder, v sl sol alechol and HOAc On adding alcoholic HCl to its ethereal solution it is changed to the isomeric nitroso dinaphthyl amine CieHe(NO) NH.CieH,

or C₁₀H₀<NH(C₁₀H₇)>O [169°] (Fischer a Hepp, B 20, 1248)

(aß) Di-naphthyl amine NH $<_{C_{1a}H_{76}}^{C_{1e}H_{76}}$ [111°]

Formed by heating a mixture of (β) -naphthol and (a)-naphthylamine with CaOl, or ZnCl..

Preparation - A mixture of (3)-naphthol (100 pts), (a)-naphthylamine (100 pts), and CaCl₂ (200 pts), is heated for 8 hours to 280°, the yield is 70 pts (Benz, B 16, 17). colourless prisms Soluble in benzene, alcohol, and ether, sparingly soluble in petroleum-ether

Picric acid compound $NH(C_{10}H_7)_2(C_0H_2(NO_2)_2OH)$ [178°], small dark brown needles

Acetyl derivative $NAc(C_{10}H_7)_2$ Di-(β)-naphthyl amine $NH(C_{10}H_7)_2$ [171°].

(471°) (Ris, B 20, 2619)

Formation.—1 Together with (8) naphthylamine by heating (3) naphthol with ammonia zinc chloride at 200° (Merz a Weith, B 13, 1800) —2 In small quantity by heating (3)-naphthol with ammoniscal CaCl₂—3 By heating (8)-naphthylamine with CaCl, or ZnCl.

Preparation -1 By heating a mixture of (β)-naphthylamine (100 pts), (β) naphthol (100 pts), and damp CaCl₂ (200 pts) for 8 hours at 275°, the yield being good (150 pts) (Benz, B 16, 9) —2 By passing HCl into fused (β)-naph thylamine at 180°, the yield being quantitative

(Klopsch, B 18, 1585)

Properties —White silvery leaflets, sol benzene and HOAc, sl sol hot alcohol Its solutions

exhibit blue fluorescence

Reactions -1 Conc HClAq at 150° has no action, but at 200° it forms $(\hat{\beta})$ naphthol and (β) naphthylamine (Ris, B 19, 2016) —2 Am moniacal ZnCl₂ and NH₄Cl at 370° forms (β)naphthylamine $(C_{10}H)_2NH + NH_2 = 2C_{10}H_7NH_2$. 3 Bromine in HOAc forms a tetra bromo deri vative C20H11Br4N [246°] Bromine and AlBr3 form C20H, Br, N [over 300°] (R18, B 20, 2621) -4 S2Cl2, acting on its benzene solution at 35°, forms two isomeric imido di-naphthyl disulphides NH CloH_e S₂, one crystallising from benzene in plates [205°], and the other in needles [220°] (Kym, B 21, 2807) — 5 Phosgens acts in the cold, forming (C₁₀H_e)₂N COCI [173°] (Kuhn a Landau, B 23, 811, cf Kym, B 23, 427) This chloro formyl derivative is v sl sol cold alcohol, v sol benzene, and reconverted into di-(β) naphthylamine by alcoholic potash

Salts -B'HCl, white crystalline pp -B'2C_sH₂(NO₂)₃OH [165°] Brown needles Acctyl derivative (C10H7)2NAc [115°]

Small colourless needles

Benzoyl derivative (C, H,)2NBz [1570]

Large needles (Klopsch, B 18, 1585)

Nitrosamine $(\mathbf{C}_{10}\mathbf{H}_{7})_2\mathbf{N}\ \mathbf{NO}$ [140°] Needles, m sol alcohol and ether, v sol benzene (Ris, B 20, 2622)

References - Bromo-, Bromo NITRO , CHLORO , IODO, IODO NITRO, and NITRO NAPHTHYLAMINE (a) - NAPHTHYLAMINE (a) - SULPHONIC ACID C₁₀H₉NSO, i.e. C₁₀H₈(NH₂)(SO₈H) [1 4] Naphthionic acid. S. 022 at 15°

Formation -1 By boiling nitro naphthalene (1 pt) with alcohol (5 pts) and aqueous ammo nium sulphite (5 pts of SG 124), and main taining an alkaline reaction by frequent addition of ammonium carbonate (Piria, A Ch [3] 31, 217, A 78, 31) -2 By heating the acid sul phate of (a)-naphthylamine (Nevile a Winther, C J 87, 632, Witt, B 19, 55)—3 By heating (a) naphthylamine (1 pt with H₂SO₄ (4 pts) at 120° for an hour (Schaal a Schmidt, B 7, 1368, Erdmann, A 247, 313)—4 By heating (a) naphthylamine with KHSO₄at 230° (Bischoff, B 23, 1913)—5 By reducing the corresponding nitro-naphthalene sulphonic acid by ammonium sulphide (Cleve, B 28, 961)

Properties -Small needles (containing sag)

(from hot water), blackened by heat without melting V sl sol alcohol, almost insol water. Not affected by boiling aqueous acids or alkalis Dilute solutions of its salts exhibit violet fluorescence The azo- colouring matters (e g Congo red), formed by its combination with diazo- compounds give on reduction o naphthylene-diamine sulphonic acid, proving that they are ortho-azo-compounds, and hence that the HSO, group occupies the para- position to the NH₂ (Witt, B 19, 1719)

Reactions -1 Split up by water at 160° into naphthylamine and H_2SO_4 (N a W) -2 Chro mic acid mixture forms a brown resinous product—3 Benzoic aldehyde, acting on its sodium salt forms C₆H₅ CH N C₁₀H₆ SO₂Na, crystallising in yellow plates, v sl sol cold water (Erdmann, 1 247, 325) -4 Succinic acid heated with its K salt at 170° forms C2H4 C2O2 N C10H8 SO2K, crystallising from water or dilute alcohol small needles (containing 2aq) (Pellizari, A 248, 157) -5 Phthalic anhydride heated with the K salt at 160° forms C.H. C.O. NC.H.SO.K, crystallising from hot water in small needles (containing 3aq) (P) -6 On displacing NH₂ by Cl, and distilling the resulting chloro naphthalene sulphonic acid with PCl, there is formed (1,4)-di chloro naphthalene

Salts - KA' small micaceous lamine, v. sol water and alcohol, sl sol KOHAq monoclinic prisms -BaA' 8aq -CaA', 8aq, monoclinic crystals, v sol water, almost insol alcohol —MgA'₂8aq monoclinic prisms —MgA'₂10aq —PbA'₂2aq, needles, sl sol water —ZnA'₂xaq —CuA'₂—AgA'aq crys talline grains —AgA'N₂H₅2aq

 $A mide C_{10}H_6(NH_2) SO_2NH_2$ [206°] Formed by reducing the amide of (1,4) nitro naph-

thalene sulphonic acid with HI in HOAc and P (Cleve, B 23, 961) Needles (from alcohol) -B'HCl colourless needles, v sl sol water

Acetyl derivative of the amide C.H.(NHAo) SO₂NH₂ [241°] Small needles (a) Naphthylamine (a') sulphonic acid

C₁₀H₂(NH₂)(SO₂H) [1 4'] S 1064 at 15° Formatron—1 By reducing (a) nitro naphthalene sulphonic acid by ammonium sulphide (Laurent, Cleve, Bl [2] 24, 511) -2 Together with naphthionic acid by adding (a)-naphthylamine hydrochloride (1 pt) at 0° to (2 pts of) fuming H₂SO₄ (containing 25 pc additional SO₄) (Witt, B 19, 578, Mauzelius, B 20, 3401) 3 Together with a small quantity of the (1, 4) acid from the acetyl derivative of (a) naphthylamine and fuming H₂SO₄ (Erdmann, A 247, 315, G Schultz, B 20, 3161, cf Lange, B 20, 2940)

Properties - Needles Solutions of its salts exhibit green fluorescence, and reduce AgNO. on warming Auric chloride, FeCl, and CuSO, colour its solution red, and suffer reduction By boiling its diazo- compound with HCl a chloro naphthalene sulphonic acid is obtained, the K salt of which on distillation with PCl, yields (γ)-di-chloro naphthalene [107°] (M). Benzoio aldehyde, acting on its sodium salt, forms C.H.OH N C.H.SO.Na, crystallising in pearly plates, decomposed by boiling water (Erdmann, A. 247, 826)

Salts -KA'aq needles or prisms, v e sol. water -NaA'aq plates (C) or needles (M).-

NaA'5aq plates (W) — BaA'₂8aq (W) — BaA'₂6aq (Ü, M)—CaA'₂6aq (W) pearly plates, v e sol water—CaA'₂9aq (C, M) tables, v sol hot water—MgA'₂8aq plates, v sol water—PbA'₂4aq 'nodules—ZnA'₂9aq needles, m sol cold water—AgA'₂

Amide [260°] Tables Yields an acetyl derivative [232°] and a discetyl derivative [200°] (Ekborn, B 23, 1119) -B'HCl -B'H2SO.

(a)-Naphthylamine peri-sulphonic C₁H_{*}(NH_{*})(SO_{*}H) [1 1] Naphthylamine sulphonic acid S S 42 at 100°, 0207 at 21° Formed, together with the (1,4') acid from naphthalene (a) sulphonic acid by nitration and reduction (Mensching, Schöllkopf's Aniline Co. G P 40,571, G Schultz, B 20, 3162) Formed also, together with the (1,4') acid, from (a)nitro-naphthalene by sulphonation and reduc-tion (Cleve, B 20, 1535) White needles (from water) or tufts of needles (from HOAo) sodium salt is less soluble than that of the presolution violet The diazo- compound treated with PCl, gives $C_{10}H_{s}ClSO_{s}$, crystallising in yel low needles [175°] —NaA' S 2 67 at 100°, 1 13 at 24°—KA' Plates S 14 9 at 100°, 3 56 at 19° (Erdmann, A 247, 306)

Anhydride C10H6 SO2 [167°] Small crystals, v sl sol water (Cleve)

(a) Naphthylamine (δ) sulphonic acid $C_{10}H_{6}(NH_{2})(SO_{3}H)$ [1 2' or 3'] S 2 at 15°, 7 at 100° Obtained by heating (a) naphthylamine (1 pt) with conc H SO, (5 pts) at 125°-130° for 8 hours until the naphthionic acid at first formed has disappeared (Hir-ch B 21, 2370) Plates, sl sol water and alcohol, insol ether and benz ene The K salt is crystalline, and sl sol cold Gives, on treatment with HNO, and HNO,, di nitro naphthol sulphonic acid isomeric with naphthol yellow S

(a) Naphthylamine 'β'-sulphonic acid $C_{10}H_6(NH_2)(SO_3H)[1 3']$ Formed, with its (γ) and (θ) isomerides, from naphthal ene (B)-sulphonic acid by successive nitration and reduction (Cleve, Bl [2] 26, 447, B 20, 1535) Slender needles (containing 2aq) or anhydrous tables, sl sol cold, v sol hot, water thin tables - KA' aq needles -NaA' 4aq MgA'₂ 10aq rhombohedra — BaA', aq needles, m sol water - CaA', 7aq rhombohedra

Anhydride $C_{10}H_6 < _{SO_o}^{NH} > [180^\circ]$ Formed by treating the chloride of ' $\tilde{\beta}$ ' nitro naphthalene (B) sulphonic acid with HI and HOAc needles, v sl sol HOAc

(a)-Naphthylamine (γ) sulphonic acid $C_{10}H_{2}(NH_{2})(SO_{2}H)$ [1 3] Formed, with isomerides, from naphthalene (β) sulphonic acid by nitration and reduction (Cleve, B 19, 2181, 21, 3271) Small needles, sl sol water Gives rise to a di-chloro-naphthalene [61°]

Salts — NaA' scales, v sol water — BaA', aq thun plates, v sol water — PbA's: prisms — AgA'aq minute needles

Amide Ci, He(NH2) SO, NH2, aq. [181°].

Needles — B'HCl prisms, sl sol cold water.

With potassium cyanate it forms NH. CO NH C. H. SO. NH CO NH. [273°].

amide Acetyl derivative of C,H (NHAc) SO,NH2. [221°].

Anhydrade C, H SO, [124°] Formed from (γ)-nitro naphthalene (β) sulphonic chloride, HOAc, and HI (Cleve, B 20, 1536) Lemonyellow needles, v sl' sol HOAc and alcohol.

(a)-Naphthylamine (θ) -sulphonic acid $C_{10}H_s(NH_2)(SO_sH)$ [12'] Formed, with isomerides, from naphthalene (β) sulphonic said by nitration and reduction (Cleve, Bl [2] 29, 415, B 21, 3264) Crystals (containing aq) rise to di chloro-naphthalene [61°] Its alcoho are solution yields with nitrous acid a deep violet

dye SO₃H C₁₀H₆ N₂-C₁₀H₃(NH₂)SO₃H 2½aq
Salts —NaA'½aq thin needles, v sol water
—CaA', 2aq powder, v sol water, turning red
in air —BaA', flat needles —ZnA', 4aq needles

Amada C H NH | SO NH | [1812] Needles

Amide C₁₀H_c(NH₂) SO₂NH₂ [181°] Needles. BHClaq —B'HI aq Yields the urea derivative NH, CO NH C₁₀H, SO₂ NH CO NH₂ [225°] Acetyl derivative of the amide

of the amide C₁₀H_•(NHAc) SO₂NH₂ [213°]

Anhydride C₁₀H₆ NH [173°] Formed from (θ) nitro naphthalene (β) sulphonic chlorade, HOAc, and HI (Cleve, B 20, 1536) Yellow needles, sol boiling Ac2O

(β) Naphthylamine 'α'-sulphonic acid C₁₀H_e(NH_e)(SO₃H)[2 1'] *Badische acid *059 (Forsling)

Formation—1 By heating (3) naphthylamine (1 pt) with cone H₂SO₄ (3½ pts) at 100°— 105° for δ or 6 hours there is obtained a mixture of the 'a,' ' β ,' (γ), and (δ) sulphonic acids of (8) naphthylamine in the proportion of about 50 pc of the 'a' acid, 40 pc of the ' β ' acid, 5 pc of the (γ) acid, and 5 pc of the (δ) acid (Green, C J 55, 35, cf Badische Anilinfabrik, G P 14,612, 20,760, Dahl, G P 29,084, 32,271, 32,276) The same mixture heated at 120° gives a greater quantity of the 'B' acid, and less of the 'a' acid Fuming sulphuric acid (20 pc SO_s extra) at 70° - 80° gives 30 p c of the 'a' and 70 p c of the (γ) -acid (β) Naphthylamine sulphate, shaken with cone H_2SO_4 for three days in the cold, yields a similar mixture (Dahl) but on heating (8) naphthylamine with conc H,SO, for an hour at 160° the 'B' and (8) acid are formed ın about equal quantities (Bayer a Duisberg, B 20, 1426, G Schultz, B 20, 1358) -2 By heat ing the (B) naphthol'a' sulphonic acid (of Bayer) with ammonia in a closed vessel (Pfitzinger a Duisberg, B 22, 396, cf Landshoff, B 16, 1931)

Properties — Needles or broad tables, v sl sol water, insol alcohol Solutions of its salts Solutions of its salts

exhibit blue fluorescence

Reactrons -1 Yields naphthalene (a) sul phonic acid when its amido- group is removed by the diazo-reaction (P a D , Nietzki a Zübelen, B 22, 453) -2 Yields by Sandmeyer's method a bromo-naphthalene sulphonic acid which can be converted into di bromo naphthalene [75°] (Forsling, B 22, 619) -8 Yields by Skraup's method (β)-naphthaquinoline sulphonic acid, which may be exidised to $\langle {}^{CO}_{C_sNH_s} \rangle C_sH_s$ SO_sH,

showing that the naphthylamine sulphonic acid is heteronucleal (Immerheiser, B, 22, 402, 412, of Armstrong a Wynne, C J. Proc 4, 108, 5,

49) -4 Heating with H₂SO₄ (8 pts) at 160° for 11 hours converts it into a mixture of the '8 and (3) isomerides (Weinberg, B 20, 3353) -5. Reacts with diazobenzene sulphonic acid, forming a yellow diazo amido- and not an azo- compound (Witt, B 21, 8488) -6 On conversion into the corresponding chloro naphthalene sulphonic acid and treatment of this with PCl, there is formed di-chloro naphthalene [61 5°]

Salts (Forsling, B 20, 2099) — NaA' plates, v. sol water, insol alcohol — KA' aq tables, v sol water — NH,A' large prisms, v sol water —BaA', 4aq columns, v e sol warm water —BaA', 4aq columns, v e sol warm water S 4 35 in the cold —CaA', 6aq tables. S 9 09 in the cold —MgA', 3 aq nodules, v e. sol water — ZnA', 6 aq columns — PbA', needles —CuA', crystalline powder —AgA'
(\$\beta\$) Naphthylamine '\$\beta\$' sulphonic

 $C_{10}H_6(NH_2)(SO_8H)$ [2 3'] 'Brönner's acid'

Formation —1 By heating the corresponding (Schaffer's) (8) naphthol sulphonic acid with ammonia under pressure (Farbfabrik vormals Brönner, G. P. 22,547), or by passing a current of ammonia over the potassium (B) naphthol sulphonate at 200° – 250° (Landshoff, B 16, 1931, Green, B 22, 723) —2 Together with the ' α ,' (γ), and (δ) isomerides by heating (β) naphthylamine (1 pt) with conc H₂SO₄ (3 pts) at 105° (Bayer a Duisberg, B 20, 1426, Green, C J 55, 35)—3 By heating (θ) naph thylamine with KHSO, at 230°, the yield being 60 pc of the theoretical (Bischoff, B 23, 1914)
4 The chief product obtained by heating (B)naphthylamine acid sulphate at 200°

Properties — Plates or flat needles, sl sol warm water (Schultz, B 20, 3158) According According to Forsling the laminar crystals contain aq Its solution exhibits blue fluorescence Yields, by conversion into diazo naphthalene sulphonic acid and application of Sandmeyer's reaction a chloro naphthalene sulphonic acid whence PCl.

forms C₁₀H₆Cl₂ [136°]

Salts (Forsling, B 20, 76) -NH, A'aq large thin plates, v sl sol water, forming a solution exhibiting violet fluorescence (Green) -NaA'2aq flat needles S 2 5 at 15° -KA'aq long needles S 24—BaA', 6aq needles S 22 at 15°—CaA', 6aq lamınæ S 44 ın the cold -MgA', 6aq laminæ or broad needles -PbA', 2aq v sl sol water - ZnA', 4aq sl sol water -AgA' aq powder CuA'24aq

(β) Naphthylamine (γ) sulphonic acid $H_s(NH_2)(SO_3H)$ [2 4'] Dahl's acid $C_{10}H_6(NH_2)(SO_3H)$ [2 4'] S 077 in the cold (F). Formed by sulphonating (β) naphthylamine, and is the chief product when the sulphonation is carried out at 15° to 20° (Dahl, G P 32,276, Forsling, B 20, 2099, Claus, J pr [2] 39, 315) Small plates or needles, insol alcohol Its solutions show blue fluorescence May be converted into di chloro naphthalene [48°] Conc H₂SO₄ (3 pts) at 160° converts it into a mixture of the 'B' and (8) isomerides (Weinberg, B 20, 3353)

Salts -xNH,A' exceedingly soluble tables KA' aq rhombohedra, v e sol water —NaA' 5aq tables, v e sol water -BaA'2 22aq nodules, v e sol water —CaA', 11aq needles S 9
the cold —AgA', 8aq crystalline
(β) Naphthylamine (δ) sulphonic acid 8 9 09 m

C10H6(NH2)(SO3H) [2 2'] (β)-Naphthylamne sulphonic acid F. Bayer's acid \$ 2857.

Formation. - 1. Together with the 'B' isomeride, by heating (3)-naphthylamine with H2SO4 at 160°-170° (Bayer a Duisberg, B 20, 1426, 3158, Schultz, B 20, 1858, 8161) It is also formed when the sulphonation is conducted at temperatures between 105° and 160°, the quantity increasing with the temperature (Green, C J 55, 86) -2 By heating the corresponding (β)naphthol sulphonic acid with ammonia at 200° (Weinberg, B 20, 2908, Erdmann, B 21, 637) or by heating naphthalene 'a' disulphonic acid with NaOH at 250°, and afterwards with NH,Cl (Weinberg, B 20, 2906, 3353) -3 By heating the 'a' or (γ) isomeride with H_2SO_4 at 160° (B a D)

Properties -Long silky needles (containing aq), m sol hot water nearly insol cold water On boiling with water the needles change to an almost insoluble crystalline powder With tetraazo diphenyl it gives a yellowish red colouring matter (5-purpurin) Yields by the diazo reac tion the (B) naphthol sulphonic acid of Weinberg, which by fusion with NaOH is converted into dioxynaphthalene [129°] Gives rise to (8)

di chloio naphthalene [114°]

Salts -KA' needles, v sol water NaA' 4aq white needles (from water) or plates (from hot 90 p c alcohol), v e sol hot water, S 14 in cold water, v sol hot spirit (90 pc) (difference from 'a' isomeride) - NHA small plates, m sol water —BaA' 243aq plates, sl sol cold water (difference from (γ) isomeride) — MgA', aq white needles (B a D) — MgA', 5aq (W) -CaA'₂ 6aq plates, with blue fluorescence S 38 at 15°

(a) Naphthylamine v sulphonic acid C10H, NHSO, H Thionaphthamic acid Formed, together with the (1,4) acid, by the action of ammonium sulphite on (a) nitro naphthalene (Piria, A 78, 54) The free acid, liberated from its salts, splits up at once into naphthylamine and H₂SO₄—KA' pearly plates, v sol water, sl sol KOHAq — NH₄A' plates, sol water and alcohol —BaA'₂Saq plates — PbA'(OAc)

(a) Naphthylamine 'a' disulphonic acid
C₁₀H₂NS₁O₆ te C₁₀H₃(NH₂)(SO₃H)₂ [1 3 3']
Formed by reducing (a) nitro naphthalene 'a'-

disulphonic acid by ammonium sulphide (Alén, Crystals, v e sol water and Bn 2, 407) alcohol, insol ether and benzene Yields (a)naphthylamine on treatment with sodium amal gam - NH, HA" 2aq (?) slender needles -KHA' 3aq needles, m sol hot water - CaA" 5aq -BaA" 4aq tables, m sol water -PbA" 4aq (?)
(a) Naphthylamine '\$' disulphonic acid

C₁₀H₃(NH₂)(SO₃H)₂ [1 3 2'] Obtained by reducing (a) nitro naphthalene 'B' disulphonic acid Small needles (from water), v sol water, sl sol alcohol Yields (a) naphthylamine on treatment with sodium amalgam -NH,HA" needles, m sol hot water -KHA" needles --BaA" aq minute needles, sl sol CaA" 2aq water —PbA

(a) Naphthylamine (δ)-disulphonic acid C₁₀H₂(NH₂)(SO₂H)₂[1 1' 4] Naphthylamine disulphonic acid S (Schöllkopf's G P 40,571) Formed by sulphonating (1, 1') naphthylamine sulphonic acid — Na₂A"2aq long needles (Bernthsen, B 23, 8090)

C₁H₂(NH₂)(SO₂H)₂[1 8 1'] Formed have naphthalana and the second secon acid Formed by heating naphthalene with conc H.SO, at 90° and fuming

H₂SO₄ at 100°-120°, then nitrating, and reducing the product (G P 45,776, 46,953, Bernth-Formed also from naphthalsen, B 22, 3328) ene (as) disulphonic acid (corresponding to C₁₀H₀Cl₂ [48°]) by nitration and reduction (Ewer a Pick, Monit scient 1889, 604, cf Armstrong a Wynne, C N 54, 255) Colourless scales (containing Saq), v e sol warm water -NaHA" 2aq needles or thin prisms, sl sol cold water — Na₂A" 6aq needles or prisms, v e sol water — BaA" 3aq — BaA" 4aq flat needles, v sol hot, m sol cold, water -Ba(HA"), 5aq minute needles, sl sol cold water

(a) Naphthylamine disulphonic acid

 $C_{10}H_s(NH_2)(SO_sH)_2[142']$ S 7 at 20° , 5 at 100° Formed, together with two isomeric acids, by sulphonating (a) naphthylamine (1 pt) with H_2SO_i (containing 25 pc SO_i extra) (5 pts) at 120° The acids are separated by treatment of the lime salts with dilute alcohol, which dissolves the salts of the two isomeric acids (Dahl & Co. G P 41,957, Armstrong a. Wynne, C J Proc 6, 125) Formed, together with a smaller quantity of the following acid, by treating (a)-naphthylamine 'a'-sulphonic acid (1 pt) with H.SO, containing SO₄ (1½ pts) at 30° Groups of needles, insol 85 p c alcohol Its solutions and those of its salts exhibit blue fluorescence

Salts -K2A" 3aq - Na2A" 3aq v sol water

CaA'2 aq v sl sol water

(a) Naphthylamine disulphonic acid

 $C_{10}H_3(NH_2)(SO_3H)_2[1 4 3']$ S 17 at 20° Formed in the preparation of the preceding, from which it may be separated by extracting the mixed cal-cium salts with dilute alcohol Alcohol of 90 p c extracts the salt of a third isomeride, sub sequent treatment with alcohol of 85 p c extracts the present acid Needles, insol alcohol, v sol boiling alcohol of 85 pc The calcium salt is v sol water, insol alcohol of 90 pc The K and Na salts are v sol water Solutions of the acid and its salts exhibit blue fluorescence

(B) Naphthylamine 'a' disulphonic acid C₁₀H₁(NH₂)(SO₃H)₂ [2 3 3'] (\$\beta\$) Naphthylamine R-disulphonic acid Formed by heating the corresponding (8) naphthol R disulphonic acid with ammonia Readily yields dyes with diazo salts

(β) Naphthylamine (γ) disulphonic acid $C_{10}H_1(NH_2)(SO_1H)_2$ [2 1'3] (β) Naphthylamine G disulphonic acid Formed by heating the corresponding (\$) naphthol G disulphonic acid with Formed also by heating (3) naphammonia thylamine sulphate (10 kilos) with H₂SO₄ (30 kilos containing 25 p c SO, extra) at 110°-140° (Gans a Co, G P 35,019) V sol water, m sol alcohol Does not react with diazo-compounds (G Schultz, B 21, 3487) The salts are v sol. water

(B) Naphthylamine disulphonic acid

C₁₀H₃(NH₂)(SO₄H₁, [2 1 3] Formed, together with the (2, 1', 3') acid, from (2, 3')-naphthylamine sulphonic acid and H₂SO₄ (with 20 p c. SO₂) at 20° (Armstrong a Wynne, C J Proc 6, 130) Needles Yields C₁₀H₂Cl₂ [92°]

(β) Naphthylamine disulphonic acid $C_{1e}H_{1}(NH_{2})(SO_{2}H)_{2}$ [2 3' x] Formed by heating (Brönner's) (β)-naphthylamine 'β'-sulphonic acid at 160° to remove water of crystallisation, adding furning H₂SO₄ (4 pts) and heating at 110° (Forsling, B 21, 3495) Possibly identical with the preceding soid. White needles, v. c. sol water, sl. sol alcohol Its dilute aqueous solution fluoresces blue It gives rise to a tri-

chloro-naphthalene [91°

Salts —K.A" 2aq large needles, v so water —KHA" aq needles, sl sol cold water large needles, v sol $NaHA''2aq - Na_2A''$ long needles $-(NH_4)_2A''aq$ monoclinic crystals -NH,HA" - *CaA" (β)-Naphthylamine disulphonic acid

H_s(NH₂)(SO₃H)₂ [2 1 4'] Formed, together with a greater quantity of the (2, 2', 4')-isomeride from (2,4') naphthylamine sulphonic acid and H₂SO₄ (with 20 pc SO₃) at 20° (A a W) Yields C₁₀H₃Cl₂[78°]

(β)-Naphthylamine disulphonic acid $C_{10}H_{4}(NH_{2})(SO_{2}H)_{2}$ [2 2' 4'] Formed as above. Yields $C_{10}H_{5}Cl_{1}$ [80°]

(β)-Naphthylamine disulphonic acid $C_{10}H_{5}(NH_{2})(SO_{3}H)_{2}[2\ 3\ 2']$ Formed from the corresponding naphthol disulphonic acid

D1-NAPHTHYL-ANTHRYLENE C22H12 18 C,HC

O₁₀H₀O (?). [270°] Formed by distilling di-

naphthyl-acetylene, or by distilling (β) di naphthyl-tri-chloro-ethane (1 pt) with ZnO (15 pts) (Grabowski, B 11,302) Large leaflets (by sublimation) — $C_{22}H_{12}C_{6}H_{2}(NO_{2})_{3}OH$ crystals (from chloroform)

NAPHTHYL ARSENIOUS ACID Described as Naphthalene arsonic acid, vol 1 p 322

NAPHTHYL-BENZAMIDINE C,HIN, 20 C.H.C(NH) NHC10H, [141°] Formed by heating (a) naphthylamine hydrochloride with benzontrile at 200° (Bernthsen a Trompetter, B 11, 1757) Tables (from alcohol), may be sublimed—B HCl white prisms—B'₂H₂PtCl₆ yellow needles -B'H,C,O, prisms, sl sol water -Chromate yellow pp
(a) NAPHTHYL-BENZYL AMINE

C,,H,,N s.e C₁₀H₇.NH CH₂Ph [67°] Formed from (a)naphthylamine and benzyl chloride (Froté a

Tomması, Bl [2] 20, 67)

(β)-Naphthyl-benzyl-amine C₁₀H, NH CH₂Ph r68°) [686] Formed by reducing C₁₀H, N CHPh (Kohler, A 241, 358) Prisms

Netrosamine C, H, N(NO) CH, Ph [112°]

Yellow needles, sol alcohol and ether

(a)-NAPHTHYL - BENZYLIDENE - AMINE C₁₀H₇N CHPh [73°] Formed from (a)-naph thylamine and benzoic aldehyde or hydrobenzamide (Lachovitch, M 9, 695, cf Papasogli, A 171, 138) Yellow needles (from alcohol)

(β)-Naphthyl-benzylidene-amine Resembles the preceding in preparation and properties (Claisen, A 237, 261)

NAPHTHYL BENZYL KETONE & BENZYL

NAPHTHYL KETONE

NAPHTHYL BENZYL OXIDE v BENZYL NAPHTHYL OXIDE

NAPHTHYL BROMO-METHYL KETONE C₁₈H₂BrO s.e O₁₀H₄, CO CH₂Br Obtained by adding bromine (9 5 g) to a solution of naphthyl methyl ketone (10 g) in CS₂ (Pampel a Schmidt, B 19, 2898) Pungent oil

(a)-NAPHTHYL CARBAMATE C₁₁H₂NO₂ te [158°] Formeu 1100 O NH, (Gattermann, A 244, C₁₀H, O CO NH, [158° naphthol and ClCO NH

43). Needles (from alcohol)

(6) Naphthyl carbamate [187°] (β) naphthol and ClCONH, (G). Long needles, almost insol. water, v. sol alcohol and ether.

(a)-NAPHTHYL-CARBAMIC ACID Ethyl ether C₁₃H₁₃NO₂ se C₁₆H₂NH CO₂Et [79°] Formed from (a) naphthylamine and ClCO₂Et (Hofmann, B 3, 657) Needles, insol water

Isopropyl ether C10H7NH CO2Pr [78°] From (a) naphthylamine and ClCO2Pr (Spica. G 17, 168) Groups of needles, sl sol water

(β) Naphthyl-carbamic acid Ethylether C₁₀H,NH CO₂Et [73°] Formed from (β) naphthylamine and ClCO₂Et (Cosiner, B 14, Needles, insol hot water, v sol alcohol

Isopropyl ether C10H,NH CO2Pr [70°]

Needles, sol alcohol and ether (S)

D1-(β) naphthyl carbamate Methyl ether
(C₁₀H₁)₂N CO₂Me [114°] Formed from d1-(β) Methyl ether naphthylamine and ClCO2Me at 155° (Ris, B 20, 2620) Needles (from alcohol and ether), v sol cold alcohol and ether

(a)-NAPHTHYL-CARBAMINE C,H,N 1 e C₁₀H, NO Formed from (a) naphthylamine, chloroform, and alcoholic KOH (Liebermann, B

16, 1640) Solid, v sol alcohol

(β) Naphthyl-carbamine C₁₀H, NC Formed from (β) naphthylamine, chloroform, and alcoholic potash (Liebermann, B 16, 1640) Needles, sol alcohol, ether, and benzene

(a)-NAPHTHYL semi CARBAZIDE CuHiN3O te CoH, NH NH CO NH2 [231°] Formed by heating (a) naphthylamine hydro chloride with urea at 140° (Pinner, B 21, 1219) Thin plates (from boiling isoamyl alcohol), insol

water and ether, sl sol dilute alkalis

(β)-Naphthyl-semi-carbazide [225°] (P), [221°] (H) Formed like its isomeride, and also by mixing equivalent quantities of (β) naphthyl amine hydrochloride and potassium cyanate in aqueous solution (Pinner, B 21, 1223, Hillring haus, B 22, 2657, Hauff, A 253, 28) Silky plates, sl sol hot water, v sol hot alcohol Reduces Fehling's solution With HClAq at 140° it yields a naphthazine

DINAPHTHYL-CARBAZOLE, so called, 18

described as Imido DINAPHTHYL

(a) NAPHTHYL CARBINOL C"H'O C₁₀H, CH₂OH Naphthobenzyl alcohol [60°] (301° cor) at 715 mm Formed by warming (a)-naphthyl carbinylamine hydrochloride with aqueous NaNO₂ (Bamberger a Lodter, B 21, 258) Long needles, v e sol ether and alcohol, sol cold water Yields (a) naphthoic aldev si sol cold water hyde on oxidation with chromic acid mixture

(β) Naphthyl-carbinol C₁₀H₇ CH₂OH [80 5°] Resembles the preceding in mode of prepara tion and properties (Bamberger, B 20, 1118)

Tri naphthyl-carbinol C₃₁H₂₂O i e ₆H₇)₂C OH Formed from naphthalene, (C₁₆H,), O OH Formed from naphthalene, C(NO₂)Cl₂, and AlCl₃, the product being boiled with water (Elbs, B 16, 1275) Crystalline powder (from acetone), melting below 278°

sol benzene, sl sol ether, almost insol alcohol

(a) NAPHTHYL-CARBINYLAMINE O₁₁H₁₁N

s.e O₁₂H, CH₂NH₂. Menaphthylamine Naph
thobensylamine (292°) Formed, together with s-di-naphthyl ethane, by reducing the amide of thionaphthoic acid in alcoholic solution with zinc and HClAq (Hofmann, B 1, 101, Bamberger a Lodter, B 21, 256) Caustic liquid, absorbing CO₂ from the air Reduced in alcoabsorbing CO₂ from the air holic solution by Na to the tetrahydride -B'HCl long needles, sl. sol. water —B',H,PtCl, erystalline pp - B'HNO. prisms [148 bo].

Tetrahydride C_{1e}H₁₁CH₂ NH₂ (270°) at 722 mm. Obtained by reducing the nitrile of (a)-naphthoic acid CieH, CN in alcoholic solution by sodium (Bamberger a Lodter, B 20, 1707) -B'HOl. white needles, v e sol hot water -

B'.H.PtCl. yellow needles, sl sol cold water —
B'C.H.(NO.),OH needles, v sol hot water
(\$\beta\$).Waphthyl-carbinylamine C₁₀H, CH.NH.
[60°] Formed from the amide of thio-(\$\beta\$) naphthose acid C.H. CS NH, by treating its alcoholic solution with zine and HCl at 35° (Bamberger a. Lodter, B 21, 1117) Prisms, sl sol cold water, v sol alcohol It is a powerful base, ppg the hydroxides from solutions of salts of copper, sine, and lead

Salts —B'HCl [260°-270°]. Prisms, v sol alcohol and water, insol ether —B'₂H₂PtCl₆ yellow needles - B'C.H.(OH)(NO.). golden-

yellow needles, v sol hot water

Tetrahydride C,eH,1 CH2NH2. (270° cor) at 729 mm Formed by adding sodium to a hot alcoholic solution of (3) naphthonitrile (Bamberger a Boekmann, B 20, 1711) Yields an Yields an scetyl derivative [65°] (Bamberger a Helwig, B Carbon disulphide reacts forming 22, 1915) C₁₀H₁₁CH₁ NH CS SHNH₁ CH₂CO₁₀H₁₁ [128°], which on boiling with alcohol gives rise to CS(NH CH₂C₁₀H₁)₂ [143°]—B'HCl [229°]

With potas Needles, v sol water and alcohol sium oyanate it gives CO(NH CH, C1, H,), (226°) and CO(NH₂)(NHCH C1, H,) [135°] — B'₂H, PtCl, Needles — B'H, CO, white needles — B', H, SO, Prisms, v e sol water — B'C₆H₂(NO₂)₃(OH) Yellow prisms, sl sol. water

DI NAPHTHYL-TRI CHLORO-ETHANE

TRI-CHLORO DI NAPHTHYL-ETHANE

(a) NAPHTHYL CYANAMIDE O, H,NH CN [188°] Formed by heating a solution of oxy-(a) naphthyl thio urea C10H,NH CS NH OH (Tie-

mann, B 22, 1940)

Di-(a) naphthyl-cyanamide $C_{21}H_{14}N_{2}$ te H,C₁₀ N C N C₁₆H, Dr-(a) naphthyl carbinide Carbo-di (a) naphthyl imide [94] Obtained Dr-(a) naphthyl carbimide by adding HgO to a boiling solution of di (a)naphthyl thio-ures in dry benzene, the yield being c 30 p c of the theoretical (Huhn, B 19, 2405) Large prisms V sol benzene, sl sol cold ether and petroleum ether By heating with dilute alcohol it is converted into di (a) naphthyl-urea H,S passed into the boiling solution in dry benzene converts it into di-(a)naphthyl thio urea Heated with CS, at 200° it yields (a) naphthyl thiocarbimide.
Di-(8)-naphthyl cyanamide

H₁C₁₀ N C N C₁₀H, Dr (β) naphthyl-carbinide. [146°] Obtained by adding HgO to a boiling solution of di-(β) naphthyl thio ures in dry benzene, the yield being 25 pc of the theoretical (Huhn, B 19, 2406) White granular crystals. (Huhn, B 19, 2406) sol hot benzene, sl sol ether and petroleum-By boiling with dilute alcohol it is converted into di (β) naphthyl urea If H,S 18 passed into its solution in dry boiling cumene, di-(β)-naphthyl-thio-ures is regenerated With

CS_a at 200° it yields (β)-naphthyl-thio carbimide
(a) - MAPHTHYL-CYÂNATE C₁₆H,N CO
(270°) Formed in small quantity by heating C,H,N CO Formed in small quantity by heating di-naphthyl-ures with P.O., and in larger quantity by the like treatment of naphthyl carbamic ether (Hall, Pr. 9, 866, Hofmann, Pr 19, 108; C R 47, 425). Pungent liquid. With oxy-aso-

Vot. III.

benzene it forms C.H. N. C.H.O CO NHC. H. [149°] (Goldschmidt a Rosell, B 23, 492) NAPHTHYL CYANIDE v Nitrille OF NAPH

THOIC ACID

NAPHTHYL CYANURIC ACID v Cyanuruc acid in the article Cyanic acids

TRI-NAPHTHYL-CYANURATES

 $(C_{10}H_{\tau})_{\alpha}C_{\alpha}N_{\alpha}O_{\alpha}$ Formed from cyanuric chloride (Ohm) 100 Mark 100 Ma sol hot water and alcohol, m sol benzene

NAPHTHYLENE-ACETAMIDINE v NAPH-

THYLENE ETHENYL-AMIDINE

o NAPHTHYLENE DIAMINE C, H, N, t.e C_{1.}H₄(NH₂), [1 2] Dr amrdo-naphthale Amrdo-naphthylamine Mol w 158 [95°] Di amido-naphthalene

Formation -1 By reduction of p sulpho benzene azo (β)-naphthylamine with tin and HCl (Griess, B 15, 2193, Witt, B 21, 3482)— By reduction of benzene azo (\$\beta\$) naphthylamine, of (β) naphthalene azo (β) naphthyl amine, of the dioxim of (β) naphthoquinone, of (2,1) nitro-(a) naphthylamine, or of (1,2) nitro- (β) naphthylamine (Lawson, B 18, 800, 2423,
 Leuckart, B 19, 174, Lellmann a Remy, B 19, 803, Bamberger a Schieffelin, B 22, 1376)

Properties - Silvery trimetric plates (from hot water), sl sol water, sol alcohol and ether Its ethereal solution quickly turns brown. FeCl.

colours its solution green

Reactions -1 Phenanthraquinons yields naphthophenanthrazine which forms yellowish white crystals giving a scarlet solution in H2SO, 2 Phenyl cyanate in benzene solution reacts forming C₂H₃NH CO NH C₁₀H₄NH₂ [335°] and (C₂H₃NH CO NH)₂C₁₀H₄ -3 Phenyl throcarb imide unites forming (C.H.NH OS NH), CioH. [355°-360°] -4 On heating with excess of oil of mustard in alcoholic solution it yields, in like manner, salky needles of CicHe(NH CS NHC2H3)2. which decompose at 170°-200° into naphthylene thio urea and di allyl thio urea (Lellmann, B 19. 808) -5 An alcoholic solution of benzil reacts forming di phenyl naphthoquinoxaline O₁₀H₆ N CO₂H₅ [148°] (Leuckart, B 19, 174) 6 o Aldehydo-benzore acrd CHO C,H, CO,H forms C₁₀H₄ NH C C₆H₄ CO₂H, which decomposes at 280° (Bistrezycki, B 23, 1044)

Salts — B'H,Cl. [90°] Prisms or plates v sol water — B'H,SO, white plates, al. sol water — Prorate nearly insoluble powder

Acetyl derivative C10H6(NHAc) [284°] White needles

Propsonyl derivative C10H6(NHC,H,O), [192°] Formed from the base and propionic anhydride Prisms (from alcohol), insol ether

Benzoyl derivative CieHe(NHBz), [291°] Plates, al sol alcohol and HOAc (Hinsberg, A

tity of the alloyolic isomeride, by reducing naphthylene-o-diamine with sodium (Bamberger a Schieffelin, B 22, 1877). Needles, v sol alcohol, ether, and hot water. Reduces AgNO, I 1 a red colour with cold aqueous FeCl, KMnO,

oxidises it to adipic acid

Salts —B'H.Cl. [c 260°] Tables, v sol water —B"2HNO. [201°] Plates, m sol water Acetyl derivative of the tetrahydride C_{1e}H_e(NHAc)₂. [245°] Needles, ▼ e. sol al cohol, sl sol ether and cold water

ac-Tetrahydride CH CH C CH(NH₂) CH(NH₂) Formed as above CH CH C CH,---CH. (B & S) Its hydrochloride and platinochloride crystallise in needles

Maphthylene-p-diamine C₁₀H_s(NH₂)₂ [14] [120°] (G·), [118°] (B a S·)

Formation —1 By reduction of naphthalene-

azo-(α)-naphthylamine by tin and HCl (Perkin, C J 18, 173, A 137, 359, Friedlander, B 22, 587).—2 By reduction of p-sulpho-benzene azo-(a)-naphthylamine with tin and HCl (Griess, B 15, 2192) —3 By reduction of (a) nitro-(a) naphthylamine (Liebermann, A 183, 238) -4 By boiling benzene-azo-(a) naphthylamine with zincdust and water (Bamberger a Schieffelin, B. 22,

Properties — Colourless prisms or needles, sl. sol water, sol alcohol and ether Yields (a)naphthoquinone on oxidation with FeCl.

Salts -B"H2Cl2 white soluble four sided plates, nearly insol HClAq -B"H,SO, needles

Mono-acetyl derivative
C₁₀H_e(NH₂)(NHAc) Formed by reducing the acetyl derivative of (a)-nitro-naphthylamine with tin and HCl (Liebermann)—B"HCl long needles $-B''_2H_2Cr_2O_7 -B''C_6H_2(NO_2)_3OH$ yel-

Ds-acety l C1aH (NHAc) derivative [205] Formed from the base or its mono-acetyl derivative and Ac₂O (Kleemann, B 19, 334, B a S) Needles, sl sol alcohol, nearly insol water and ether

Mono-bensoyl derivative [186°] Formed by re-C₁₀H₀(NH₂)(NHBz)

CleH₄(NH₂)(NHD2) (Ebell, A 208, 326) —

Needles —B"HCl —B"HNO₄ — B"H₂SO₄

ar-Tetrahydrids CH₂CH₂C C(NH₂) CH

CH₂CH₂C C(NH₃) CH The sole product of the reduction of p naphthylene-diamine by sodium (Bamberger a Schieffelin, B. 22, 1882) Needles, resimified on exposure Yields adipic acid on oxidation with KMnO₄.—B"H₂Cl₂ crystalline powder

Acetyl derivative of the tetrahydride C₁₀H₁₀(NHAc)₂ [285°] Needles, v sl sol cold water, m sol boiling alcohol Reduces ammoniscal AgNO₂ FeOl₂ colours a solution of its hydrochloride green, changing to brown

Pers-naphthylene-diamine $C_{10}H_6(NH_2)_2[1 1]$

[670]

Formation —1 By reduction of peri di nitronaphthalene with 10dide of phosphorus and water (De Aguiar, B 3, 27, 7, 307, Beilstein a Kuhlberg, A 169, 90, Ladenburg, B 9, 1651) 2 By reducing di-mitro-(a)-naphthoic acid [265°] with tin and HCl (Ekstrand, B 20, 1353, J pr [2] 38, 263) —8 By the action of ammonia on pert-di oxy-naphthalene at 150°-800° (Erdmann, A 247, 868)

Properties — Needles (from dilute alcohol), sol water Gives a reddish-brown colour m sol water Gives a reddish-brown colour and pp with FeCl, NaNO, added to a solution of the sulphate ppts red needles of the azimide.

By the diazo- reaction it yields dichloronaphthalene [84°] Benzoic aldehyde forms

C₁₀H₀<NCH₀Ph) (Hinsberg, B 22, 861) Benzoic aldehyde forms Phenanthraquinone does not yield an azine Oxalic ether at 100° yields C₁₄H₁₂N₂O₂, crystallising from chloroform in red needles, carbonised at 195° (Aguiar)
Salts—B"H₂Cl₂ [c 280°]
B"H₂I₃—B"H₂CO₄

Small plates -

(1,4')-Naphthylene diamine C10H6(NH2) [14] [190°] Formed by reducing the corresponding di nitro naphthalene in alcoholic solu tion with tin and HCl (Erdmann, A 247, 361, cf Zinin, A 52, 362, 85, 329, Hollemann, Z [2] 1,555, De Aguiar, B 3,33, 7, 307) Formed also by heating the corresponding di oxy-naphthalene with ammonia at 150°-180°, and finally at 250°-300° (E) Thin white needles, which may be sublimed, sl sol cold water, v sol alcohol FeCl, colours its solution bluish-violet Converted by the diazo reaction into di chloronaphthalene [107°] — $B''H_2Cl_2$ — $B''H_2I_2$ —

naphtnaieue
B"H,SQ, —B"H,QQO,

Tetrahydride CH CH.—— C CH(NH,) CH,

CH CH.—— CH,

CH CH, —— CH,

CH CH, —— CH, (264°) at 60 mm Formed by the action of sodium on a solution of the base in isoamyl alcohol (Bamberger a Hoskyns-Abrahall, B 22, 944) Prisms (from ether) or needles (from ligroin), al sol hot water, v sol alcohol FeCl. gives a deep reddish-brown colour in its hot solution, but no colour in the cold Boiling K₂Cr₂O₇ gives a claret-colour Gives off NH₃ when heated This base can be separated into dextro- and levo-rotatory varieties by crystallisation of the bitartrate, for on adding a crystal of dextro rotatory comme tartrate, the lavorotatory tetrahydro naphthylene diamine tartrate crystallises out, while the mother liquor deposits the dextro-rotatory compound after long standing (Bamberger, B 23, 291) The rotatory powers of the two hydrochlorides, [a]_b are
-7° 30' and +8° 9' respectively Reactions
1 Nitrous acid at 0° forms a diazo-compound which when boiled with water yields pound which wall CH CH CH CH CH CH(NH₂) CH₂ the di acetyl derivative of which crystallises in needles [152°] (Bamberger a Bammann, B 22, 960) —2 Deazotisation and reduction by SnCl2 and HCl yields the hydrazine CH CH —— C CH(NH,) CH, OH C(N,H,) C —— CH,— CH,— 3 A dilute ethereal solution of CS, forms $C_{10}H_{10}(NH_2) NH_3S CS NH C_{10}H_{10}NH_2 [145°]$, the alicyclic amidogen entering into reaction By treatment with PbO this substance is converted into the urea CO(NH Cl. H10 NH2)2. Boiling with alcohol yields CS(NH Cl. H10 NH2)2. [155°]—4

A warm alcoholic solution of CS, forms C₁₀H₁₀ NH CS NH C₁₀H₁₀ [175°], both amidogens taking part in the reaction Salts dogens taking part in the reaction Salts B"H₂Cl₂ trimetric prisms, a bc = 574 1 906, v sol water, v. sl. sol alcohol—B"H₂PtCl₃ a prisms — B"₂H₂PtCl₃ crystalline solid—B"H₂SO₄2aq triclinic prisms Acetyl derivative C₁H₁₀(NHAc)₂. [262° cor] Prisms (from alcohol), sol ether, sl sol boiling water (2,2) Naphthylene-diamine C₁H₄(NH₂), [2 2].

[159°] (B. a. S.); [161°] (L.). Formed by heat-

ing the corresponding di oxy naphthalene [186°] of Ebert and Merz with ammoniacal CaCl, at 265° (Lange, B 21, Ref 839, Bamberger a Schieffelin, B 22, 1384). Plates (from water), \mathbf{v} sol boiling

water, alcohol, and ether

C10H0(NH2)2. (2,8')-Naphthylene - diamine [218°] Formed from di-oxy naphthalene [213 by heating with ammonia and NH, Cl at 2000-250° (Lange, B 21, Ref 839) Its salts are more soluble than those of the (2,2')-isomeride m-Naphthylene diamine C₁₂H₄(NH₄)₂[1 3]

Obtained by reducing di nitro naphthalene [144°] with tin and HCl (Urban, B 20, 973) A solution of its hydrochloride is coloured yellow by nitrous acid -B"H2Cl2 v. e sol water, m sol alcohol, insol ether

Acetyl derivative C10H4(NHAc). [156°]. Prisms, v sol benzene

Dinaphthylene-amine C₂₀H₁₂N s.c.

 $C_{10}H_{s} > NH$ (?) [159° cor] Formed by heat $ing(\beta\beta)$ dioxy dinaphthyl with ammoniscal zinc chloride (Walder, \vec{B} 15, 2173) White trimetric plates or needles \vec{V} sol ether, benzene, or acetone, insol dilute acids

Pieric acid compound $_{10}H_{18}N \ 2(C_{6}H_{2}(NO_{2})_{3}OH)$ [219° cor] blue-

black needles

[144° Acetyl derivative C20H12NAc uncor], fine white needles, v sol ether, less

sol alcohol

Trı naphthylene dıamıne CaoH, N2 $(C_{10}H_{4})_{2}N_{2}$ (?) Formed by heating a mixture of naphthylamine, naphthylamine hydrochloride, and nitro naphthalene in molecular proportions for 3 hours at 190°-220° (Salzmann a Wichelhaus, B 9, 1107) Amorphous blue black powder (containing aq), insol water and ether, forming a red solution in warm benzene Begins to decompose at 180° -B'HCl amorphous violet powder

References — Bromo-, DI-CHLORO,

ETHENYL-NAPHTHYLENE DIAMINE

o NAPHTHYLENE DIAMINE - 'a' - SUL-PHONIC ACID

C(NH,) C(NH,) C10H10N2SO 2.0 C0H . Formed, C(SO,H) CH

together with benzidine, by reduction of Congored Not isolated (Witt, B 19, 1719)
o-Waphthylene-diamine 'B'-sulphonic acid

CH CH C C(NH₄) C(NH₄) SO, HC = CH C CH = CH Obtained by reducing 'gold-brown,' an azo dye obtained from Brönner's (\$)-naphthylamine sulphonic acid, and diazobenzene (Witt, B 21,3484) Yellowishwhite crystals (from alcohol or ether), v sl sol Quickly turns brown in air K,FeCy. turns its solution first brown, then yellow FeCl. colours its aqueous solution dirty-green anthraquinone bisulphite yields, in presence of NaOAc and HOAc, naphthophenanthrazine sulphonic soid, which dissolves in H.SO, with reddish-violet colour, and which is converted by potash fusion into a eurhodol, forming in H2SC a solution coloured a pure ultramarine, turned cherry-red by water Naphthylene-diamine 'a'sulphonic acid acts in the same way, but the compound formed by phenanthraquinone dis-solves in H.SO, with bluish-violet colour, and the eurhodol with indigo blue colour, the sul-

phate being ppd as a crimson crystalline powder

o Naphthylene-diamine (γ) -sulphonic acid CH CH — C C(NH₂) C(NH₂) CH C(SO₂H) C CH — CH Formed by reduction of azo dyes prepared from (8)-naphthylamine (γ) sulphonic acid (of Dahl) (Witt, B 21, 8486) Plates, sl sol water (more soluble than the 'B'- isomeride) FeCl, colours its solution emerald green The corresponding azines are rendered violet by H2SO4, becoming orange on dilution The eurhodol gives a dark violet solution in H2SO, becoming cherry-red on dilution, the eurhodol sulphate being deposited in dirtyred flakes

o Naphthylene-diamine (δ) sulphonic acid SO, $H C = CH C C(NH_2) C(NH_2)$ Obtained by

CH CH C CH==CH reducing azo- dyes prepared from (β)-naphthylamine (8) sulphonic acid (W) Grey powder, more soluble in water than the 'B'- isomeride Occurs also in a gelatinous (? hydrated) condition, v e sol water It resembles the 'B'- isomeride in its reactions with FeCl3, with K2FeCy. and with phenanthraquinone

o Naphthylene-diamine 'a'-disulphonic acid $C_{10}H_4(NH_2)_2(SO_3H)_2$ [1 2 1' or 4' 3'] Obtained by reducing benzene azo (β) naphthylamine 'a'disulphonic acid formed from (3) naphthylamine R disulphonic acid (Witt, B 21, 3487) - NaHA" sandy crystalline powder, v sol water, forming a solution with green fluorescence FeCl, gives a green colour Yields lemon yellow sodium naphtho phenanthrazine disulphonate, which forms a bluish magenta solution in HSO, The eurhodol yields a deep greenish blue solution in H2SO4, becoming claret red on dilution

Naphthylene-diamine disulphonic acid C₁₀H₄(NH₂)₂(SO₂H)₂ Formed by reducing dinitro naphthalene disulphonic acid (Alén, Bn 3, 1025) —KHA" 3aq needles, m sol hot water — Ba(HA"), 6aq NAPHTHYLENE-BENZAMIDINE v Benz

ENYL NAPHTHYLENE AMIDINE

NAPHTHYLENE ETHENYL-AMIDINE

 $C_{12}H_{10}N_2$ s.s. [2 3] $C_{10}H_0 < NH > 0$ CH₂ [168°]. Formed by the action of cold conc alcoholic upon (β) naphthyl ethyl nitrosamine r a Hepp, B 20, 1248) Nodules (from HCl (Fischer a Hepp, B 20, 1248) Crystallises from methyl alcohol in water) prisms (containing MeOH) [75°] Sl sol hot water — B'HCl laq colourless needles, sl solwater, m sol alcohol — B'.H.PtCl, 3aq — B'H.SO, — B'C.H.(NO.),OH needles colourless needles, al sol.

Naphthylene ethenyl-amidine

[1 2] $C_{10}H_0 < N \\ NH > CMe$ Formed from the acetyl derivative of nitro (B) naphthylamine by reduction with tin and HCl (Liebermann a Jacobson, A 211, 67) Formed also by the action of cold alcoholic HCl on (B)-naphthyl-ethyl-amine (Fischer a Hepp, B 20, 2472)—B'HCl 2aq. needles, v sol water
NAPHTHYLENE-ETHYL-DIAMINE

C, H (NH2)(NHEt) [14] Formed by reducing nitroso-(a) naphthyl ethyl amine with SnCl₃ (Kock, A 243, 312) The free base is unstable. It yields (a)-naphthoquinone on oxidation — B"H₂Cl₂ [152°] Plates — B"2C₆H₂(NO₂),OH. [180°]. Needles, sl. sol. water and alcohol

DI NAPHTHYLENE - GLYCOL, so called C₂₂H₁₄O₂ to C₁₀H₆ COH (?) Formed by the action of chloroform and aqueous NaOH on (β)naphthol (Rousseau, A Ch [5] 28, 151) Small crystals, insol water and alkalis, v sl sol alcohol, HOAc, and chloroform, m sol ether

Reactions -1 Chromic acid mixture yields crystalline C₂₁H₁₂O [188°] —2 Red hot soda lime forms dinaphthyl [187°] —3 Fuming hydro chloric acid (15 pts) at 160° forms C₂₂H₁₄Cl₂O 3aq crystallising in red needles —4 With fuming hydrobromic acid it forms the corresponding C.H.Br.O Saq crystallising in lustrous green plates, whence alcoholic ammonia produces $C_{22}H_{12}(OH)(NH_2)$ crystallising from benzene in needles and forming the crystalline salts B'H2Cl2, B'₂H₂PtCl₂, and B'H₂Br₂ The compound C₂₂H₁₄Br₂O 3aq is converted by hot HOAc into C₂₂H₁₄BrOHOAc crystallising in lustrous green tables and giving off HOAc at 100° -5 Bromine in CS₂ forms orange plates of C₂₂H₁₃Br₃O-6 HIAq (S G 17) forms, on boiling, crystals of $C_{nH_{12}}I_{10}O = 7$ Dilute nutric acid (S G 12) forms $C_{2:H_{12}}(OH)(NO_3)$, which separates from HOAc as a red crystalline mass C₂H₁₂(OH)(NO₃)HOAc Boiling dilute nitric acid forms red needles of $C_{22}H_{12}(NO_3)_2$ [190°] —8 H.SO 4 (5 pts) at 100° forms $C_{22}H_{12}(OH)(SO_4H)H_2SO_4aq$ crystallising in red needles with golden lustre, and separating

from HOAc as C₂₂H₁₂(OH)(SO₄H)HOAc
Di-acetyl derivative C₂₂H C₂₂H₁₂(OAc)₂. [192 5°] Needles, sl sol alcohol, v sol C.H. Anhydride C₂H₁₂O [1985°] Formed by heating 'dinaphthylene-glycol' with PCl₅ Formed

Formed also by the action of boiling alcohol on the compounds $C_{22}H_{13}Br_{2}O$ and $C_{22}H_{13}ClO$ (v supra) Yellow needles (from benzene), almost insol cold alcohol, v sol boiling benzene Yields on reduction a compound OzH14O

(a)-DI-NAPHTHYLENE KETONE OXIDE $C_{21}H_{12}O_2$ is $C_{10}H_6 < \frac{O}{CO} > C_{10}H_6$ [240°] Formed

by boiling (a) naphthyl ethyl carbonate (Bender, Yellow prisms, sl sol. alcohol B 13, 702)

(β)-Dinaphthylene-ketone oxide (?) $C_{21}H_{12}O_2$ 1 6. $C_{10}H_6<_{CO}>C_{10}H_6$. [194°] Formed, to-

gether with (β)-naphthol, alcohol, and CO₂, by long boiling of di (8) naphthyl-di ethyl orthocarbonate (C₁₀H₂O)₂ C (OC₂H₅)₂, its formation is explained by assuming the intermediate formation, by molecular change, of (β) naphtholcarboxylic ether C₁₀H₄(OH)CO₂Et, which by elimination of H₂O and diethyl carbonate would give dinaphthylene-ketone oxide Thin colourless prisms (from benzene) V sl. sol alcohol (Bender, B 19, 2267)
NAPHTHYLENE MERCAPTAN Cl. H. S. 2 & V al. sol alcohol

C₁₀H₀(SH)₂, [181°] (G.), [174°] (E) (210° at 15 mm) Prepared by reducing the chloride of naphthalene 'a'-disulphonic acid with zinc-dust and H.SO., and extracting the product with ether (Grossean, B 23, 2370, Ebert, B. 24, 145) Pearly leaflets (from alcohol), v. sl. sol. cold alcohol and ether Its alcoholic solution gives a yellow pp with lead acetate Its alkaline solution is rapidly

oxidused by air Crystals.

Acetyl derivative. [1109]. Bensoyl derivative. [1589].

NAPHTHYLENE - DI - METHYL - DIAMINE H₆(NH₂)(NMe₂) [14] Formed by reducing nitroso naphthyl di methyl diamine or benzene azo-dimethylnaphthylamine (Friedlander, B 21, 3124) Liquid, m sol hot water

Acetyl derivative C10H6(NHA0)(NMe,) [1959

NAPHTHYLENE (a)-NAPHTHYL-DIAMINE C₂₀H₁₆N₂ 2 6 [1 4] C₁₀H₆(NH₂)(NHC₁₀H₇) Formed by reducing nitroso di (a) naphthylamine with SnCl, and HCl (Wacker, A 243, 303)

crystals (from benzene), v sol alcohol NAPHTHYLENE - NAPHTHYL - BENZAM

IDINE C27H18N2 & C6H5 C NC10H2 [1639]

Formed by reducing benzoyl-nitro di (3) naph thyl amine with tin and HCl (Ris, B 20, 2626) Slender needles (containing C,H,) [114°], m sol alcohol and ether

NAPHTHYLENE DI-NAPHTHYL-SULPH-IDE OXIDE $C_{30}H_{20}SO$ is $C_{10}H_{1}O$ $C_{10}H_{6}$ S $C_{10}H_{1}$. [111°] Formed in small quantity as a byproduct in the preparation of (a) and (β)naphtho nitrile by distilling a mixture of (a) and (B)-potassium naphthalene sulphonate with potassium ferrocyanide (Ekstrand, B 17, 2601, J pr [2] 38, 140) Long needles By K₂Cr₂O, and acetic acid it is oxidised to a compound [162°] By heating with dilute HNO, at 130°-140° it yields a body C₂₀H₁₂N₂SO₄ which crystallises from hot acetic acid in small yellow prisms [231° uncor], nearly insoluble in alcohol and CS₂.

Br and I in CS₂ yield C₃₀H₁,Br₂SO [182°]

(a)-DINAPHTHYLENE OXIDE C₃₀H₁₂O i.e

C₁₀H₀O [182°] Formed by distilling (a)maphthol (1 pt) with lead oxide (8 pts), the yield being 7 pc (Knecht a Unzeitig, B 13, 1724, A 209, 134), and, together with naphthal ene, by heating (a) naphthol at 850°-400° (Merz a Weith, B 14, 195) or distilling it with an equivalent quantity of lime (Niederhäusern, Colourless needles, msol water, B 15, 1121) sl sol alcohol, v sol ether

Picric acid compound

 $C_{22}H_{12}O$ $2C_6H_2(NO_2)_3OH$ [173°] Bed needles (β) Dinaphthylene oxide $C_{22}H_{12}O$ [155°] (K a U), [157°] (W), [161°] (M a W) VD 9 05 (obs) Formed by distilling (β) naphthol (1 pt) with PbO (8 pts) (K. a U) Formed also (α) by passing a current of air into boiling (8) naphthol (Merz a Weith, B 14, 200) and by heating di-oxy (3) dinaphthyl (1 pt) with ZnCl₂ (4 pts) for 6 hours at 270° (Walder, B 15, 2171) Silvery plates, insol water. sl sol alcohol, v sol ether

Picric acid compound C₂₀H₁₂O 2C₆H₂(NO₂)₂OH Red needles, v sol. hot benzene

References -- DI BROMO- and DI-CHLORO- DI NAPHTHYLENE OXIDE

(a) DINAPHTHYLENE OXIDE SULPHONIC ACID C20H2(SO3H)4O Prepared by sulphonating (a)-dinaphthylene oxide —A''Ba₂ 2aq needles, sparingly soluble in water with a beautiful blue fluorescence (Knecht a Unzeitig, B 13, 1725) (β) - DINAPHTHYLENE - OXIDE - TETRA

SULPHONIC ACID $O_{20}H_3(SO_3H)_4O$ Prepared by sulphonating (β) dinaphthylene-oxide. — $A^{11}Ba_2$ 2aq: tables (K. a. U.).

DINAPHTHYLENE PHENYL-AMINE PHENYL DINAPHTHYLENE AMINE

NAPHTHYLENE DISULPHOCYANIDE C₁₀H₆(SCN)₂. [78°] Formed from C₁₀H₆S,Pb, alcohol, and cyanogen chloride (Ebert a Klei-

ner, B 24, 146) Needles

(αβ) NAPHTHYLENE TOLAZINE O, H, N2 € e C_eH_s(CH_s) $C_{10}H_6$ [141°] Formed by

mixing acetic acid solutions, cooled to 0°, of (β) naphthoquinone and tolylene-o diamine (Hinsberg, B 18, 1229) Distils without decomposition at a high temperature Yellowish crys V sol alcohol, acetic acid, and benzene, insol water Dissolves in strong HCl with a brownish red colour

DI NAPHTHYLENE DI THIO DI-UREA

Octohydride CS NH C, H, NH CS [175°] Formed by boiling the tetrahydride of (1, 4'). naphthylene diamine with CS, and alcohol (Bamberger a Bammann, B 22, 951) Crystalline powder, v sol alcohol

NAPHTHYLENE-UREA C, H, N, O 1.6

 $C_{10}H_6{<_{\rm NH}^{\rm NH}}\!\!>\!\!{\rm CO}$ [c 880°] Formed from naphthylene diamine and COCl2 in toluene at 100° (Hartmann, B 23, 1048)

(aà) DI-NAPHTHYL-ETHANE C.H. (C₁₀H)₂C₂H₄ [160°] Formed, together with (a) naphthyl carbinylamine, by reducing the amide of thio (a) naphthoic acid in alcoholic solution with zinc dust and HClAq (Bamberger, B 21, 54) Hexagonal plates, v sol chloroform and benzene, m sol ether, sl sol alcohol alcoholic solution exhibits greenish blue fluorescence 1

(ββ) D1 naphthyl-ethane C10H CH2 CH2 C10H, [253°] Formed, in like manner, from thio (β) naphthoic amide (B) Plates, v sol chloroform and benzene, sl sol ether and al-Its solutions fluoresce bluish violet

References - TRI CHLORO and TRI CHLORO-TETRA NITRO DI NAPHTHYI ETHANE NAPHTHYL ETHER v

DI NAPHTHYL OXIDE

(a)-NAPHTHYL-ETHYL-AMINE C,2H,1N t & C₁₀H, NHEt Ethyl naphthylamine (303° 1 V) at 723 mm (Bamberger a Helwig, B 22, 1312) Formed by cohobating naphthylamine with EtBr (Limpricht, A 99, 117, Schiff, A 101, 90) Obtained also by reducing C₁₀H, NH CS CH, with zinc dust and HClAq (Bernthsen a Trompetter, B 11, 1756) Colourless crystals, becoming dichroic (steel blue and brown red) in light Forms a nitrosamine, which, in contact with alcoholic HCl, changes to the isomeric nitroso derivative $C_{10}H_6 < \stackrel{NEt}{N} > 0$ [133°] (Kock, A 243,310) -B'HCl [193°] -B'2H2PtCl, yellow prisms -B'HBr -B'HI four sided prisms

(β) Naphthyl - ethyl - amine C₁₆H, NHEt (805°) at 716 mm Oil (Henriques, B 17, 2663, Bamberger a Muller, B 22, 1297) Yields a red dye with diazotised sulphanilic acid gives no colour in the cold, a greenish-brown colour in warm solutions K,Cr,O, and H,SO, give a brown colour and pp —B'HCl [235°]. Plates, al sol cold water

Netrosamene CieH, NEt(NO)

Crystals Converted by alcoholic hydrogen chloride at 5° into nitroso naphthyl-ethyl amine C_eH₄ C(NO) CNHEt -B'HCl [108°] Green prisms (from benzene) (Fischer a Hepp, B. 20, **124**8, 2471)

(α) Naphthyl - di - ethyl - amıne C₁₀H, NEt₂. (291°) SG 1005 Formed by heating (a)-naphthylamine (10 g) with EtBr (15 g) and alcohol or NaOHAq at 120° (B E Smith, C J 41, 180, Friedlander, B 21, 3129) Formed also by heating (a) naphthylamine hydrochloride with Oil, v sol alcohol and ether alcohol Forms a nitroso- derivative $C_{10}H_c(NO)NEt_2$ [165°].—B'HCl silky plates, v sol hot water.—B'₂H₂PtCl₆ golden yellow plates—Sulphate: thick prisms

Ethylo rodide C, H, NEt, I [100°] Cubes Ethylo-bromide C, H, NEt, Br Tables (from water)

(3) Naphthyl-di-ethyl-amine $C_{1e}H$, NEt₂ (316° 1 V) at 717 mm Oil (Bamberger a Williamson, B 22, 1760) Yields (3) naphthylamine on heating with lime — B'HCl [175°] Tables or needles, v e sol water —B'₂H₂PtCl₆
Di (β) naphthyl-ethyl-amine 01. [95°] (O_{1.}H.).NEt

[231°] From di (8) naphthylamine and EtI at 150° (Ris, B 20, 2619) Needles, m. sol cold

alcohol, insol petroleum ether

(a) NAPHTHYL-ETHYL-AMINE TETRA HYDRIDE C₁₂H₁₇N 2 6 CH₂CH₂C C(NHEt) CH CH₂CH₂C-CH CH (287° 1 V) at 717 mm Formed by adding so dium to a solution of naphthyl ethyl-amine in isoamyl alcohol (Bamberger a Helwig, B 22, Colourless liquid, sl sol water, v al sol NaOHAq, v sol alcohol Reduces warm alcoholic AgNO, Diazobenzene sulphonic acid yields an orange dye FeCl, added to a solution of its hydrochloride gives a claret colour, changing to greenish yellow K₂Cr₂O, and H₂SO₄ give a dirty yellow pp in the cold, but in warm solutions a red colour, becoming greenish brown, further addition of K.Cr O, ppts blue black flakes KMnO, oxidises it to adipic and oxalic acids — B'HCl [118°] Prisms or needles, v sol water — B'₂H₂PtCl Plates, sl sol cold water

Netrosamene C10H11(NEt NO) Formed by adding NaNO, to a solution of the base in HClAq Yellow oil, exhibiting Liebermann's reaction Tin and HClAq reconvert it into CieHii(NEtH) When dissolved in alcoholic HCl it slowly changes to the isomeric $C_eH_s < C(NEtH)$ CH

crystallising in golden needles [119°]

ar-(\$) Naphthyl-ethyl-amine tetrahydride CH, CH, C CH C(NHEt) CH, CH, C CH CH (291 5°) at 724 mm Formed, together with the alicyclic isomeride, by reducing (β) naphthyl ethyl amine (15 g) in isoamyl alcohol with sodium (24 g) (Bamberger a Müller, B 22, 1304) Colourless oil, volatile with steam, v sol alcohol, v al sol water, insol NaOHAq Smells like piperidine FeCl, colours a warm solution of its hydrochloride reddishbrown KMnO, oxidises it to adiple acid—B'HCl [173 5°] Needles, v sol water, ppd as plates by addition of HCl—B'_*H_*PtCl, Needles. ac-(B)-Naphthyl-ethyl-amine tetrahydride

C.H. CH. CH. NHEt (267°) at 724 mm. SG. 15 998 Formed as above (B a M) Colourless oil, sl sol water, very volatile with steam FeCl. colours a warm solution of its hydrochloride reddish brown Reacts with diazobenzene nitrate, $C_{10}H_{11}$ NEt $N_2C_6H_5$ [58°] — B'HCl Prisms (from water) or needles (from forming [223 5°] CHCl,) Ppd in plates by adding HCl to its aqueous solution —B'HNO, [184°] Needles or plates, v sol hot water —B'HNO, [180°] Needles —B'₂H₂PtCl₆ [204°] Or stellate crystals —B'C₆H₂(NO₂)₃OH [204°] Orange yellow [183 5°] Needles, v sol water and alcohol

(828° Acetyl derivative C10H11 NEtAc

uncor) at 718 mm Oil

Nitrosamine C10H11 NEt(NO) Yellow oil,

▼ sl sol cold water

 $Ar-(\beta)$ Naphthyl-di-ethyl-amine tetrahydride CH, CH, C CH CNEt, (298°) at 709 mm The CH, CH, C CH CH chief product of the reduction of C, H, NEt, by sodium (Bamberger a Williamson, B 22, 1763) Liquid, al sol water Yields a red dye with p-diazobenzene sulphonic acid KMnO₄ oxidises it to adipic acid -B'HCl granules, v e sol water

 $Ac-(\beta)$ -Naphthyl-di-ethyl aminetetrahydride C.H. CH, CH NEt, Liquid, sl sol water, insol NaOHAq —B'H2CO3 white needles -B'HCl prisms, v sol water

(a) NAPHTHYL ETHYL CARBONATE $C_{13}H_{12}O_3$ is $C_{10}H_7$ OCO OEt [31°] Obtained (a)-naphthol and chloroformic ether (Bender, B 13, 702, 19, 2266) Tables, sol alcohol By heating to boiling for some time it Isplits up into (a) naphthol, a body $C_{21}H_{12}O_{2}$ [240°], which is probably a dinaphthylene-ke-

tone-oxide C₁₀H_e<0>C₁₀H_e, alcohol, and CO₂

Di-(B) - Naphthyl di-ethyl-orthocarbonate (O₁₀H₂O)₂ C (OC₂H₃)₂ (298°-300°) Obtained by the action of chloroformic ether upon (3) naphthol (Bender) White amorphous mass, melting with the heat of the hand HCl at 250° decomposes it into (β) naphthol, EtCl, and CO₂ By long boiling it is decomposed into (β) naphthol, a body $C_{21}H_{12}O_2$, which is probably a dinaphthylene ketone oxide, alcohol, and CO_2 .

(a) - NAPHTHYL - ETHYLENE C12H10 26 CicH, CH CH, Formed by the action of Na₂CO₃ on & bromo-a-naphthyl-propionic acid (Brandis, B 22, 2158) Oil, smelling like styrene Bromine in chloroform forms C₁₀H, CHBr CH₂Br [168°]

References - DI-CHLORO- and DI-CHLORO-

TETRA-NITRO-DI-NAPHTHYL ETHYLENE

DI - (a) - NAPHTHYL-ETHYLENE-DIAMINE $C_{22}H_{20}N_2$ i.e. $C_2H_4(NHC_{10}H_7)_2$ [127°] Formed from naphthylamine and $C_2H_4Br_2$ (Reuter, B 8, 23) —B"H,80,

 \mathbf{Di} - (β) -Naphthyl-ethylene-diamine $C_2H_4(NHC_{10}H_7)_2$ [158°] (M), [150°] (B) Formed, together with di-(β)-naphthyl-pyrazine tetrahydride $C_2H_4 < N(C_{10}H_7) > C_2H_4$ [228°] by the action of ethylene bromide on (β) naphthylamine in presence of sodium carbonate (Maschke, C C 1886, 824; Bischoff, B 23, 1985) Plates and needles, sl sol ether, m sol absolute alcohol.

DI-(a)-NAPHTHYL-ETHYLENE-DI-CARB-

AMIC ETHER $C_{2i}H_{2i}N_{2}O_{4}$ to $C_{2}H_{4}(N(C_{1i}H_{1})CO_{2}Et)_{2}$ [156°] Formed from $C_{2}H_{4}(NHC_{1i}H_{1})_{2}$ and $ClCO_{2}Et$ (Reuter, B 8, 25) Formed from sol alcohol

DI-(a)-NAPHTHYL-ETHYLENE DIOXIDE $C_{22}H_{18}O_2$ is $C_2H_4(OC_{10}H_7)_2$ [126°] Formed from (a) naphthol, KOH, and $C_2H_4Br_2$ (Koelle, B. 13, 1956) Plates

D1-(\$)-Naphthyl-ethylene dioxide

 $C_2H_4(OC_{10}H_7)_2$ [217°] Formed in like manner Plates, sl sol benzene and HOAc, insol water, alcohol, and ether

(β)-NAPHTHYL-ETHYL-HYDRAZINE

C₁₂H₁₄N₂ te C₁₀H₁NEt NH₂. Formed from (8) naphthyl hydrazine and EtI in EtOH (Hauff, A 253, 33) Yellow oil, v sol alcohol Reduces Fehling's solution and HgO without formng a tetrazone —B'HCl plates
NAPHTHYL ETHYL OXIDE v Ethyl ether

of NAPHTHOL

NAPHTHYL - ETHYL - NITROSAMINE v Nitrosamine of Naphthyl-Ethyl-amine NAPHTHYL DI ETHYL PHOSPHINE

 $C_{14}H_{17}P$ is $C_{10}H_{1}PEt_{2}$ (above 360°) Formed from $C_{10}H_{1}PCl_{2}$ and $ZnEt_{2}$ (Kelbe, B 11, 1501) Formed Yellow oil

Ethylo vodide C, H, PEt, I [209°] Colourless leaflets

NAPHTHYL - GLYCOCOLL v NAPHTHYL-AMIDO-ACRTIC ACID

DI-NAPHTHYL-GLYCOL v DI-NAPHTHYLENE-

NAPHTHYL - GLYCOLLIC ACID v Oxy-NAPHTHYL ACETIC ACID

(a) NAPHTHYL-GLYOXYLIC ACID C12H8O1 C₁₀H, CO CO₂H Naphthoyl formic acid [114°] Obtained by saponification of its nitrile (Boessneck, B 15, 3066, 16, 640), and by oxidation of (a) naphthyl methyl ketone by KMnO. (Claus a Feist, B 19, 3181) Needles or plates, m sol water, v sol alcohol and ether Gives a red colour on shaking with H2SO, and benzene Yields (a)-naphthoic acid containing thiophene [160°] on oxidation — OaA'₂4½ aq v sol water — AgA' white pp, v sl sol water — Amide C₁₀H₇ CO CONH₂. [151°]. Long

white needles (from alcohol)

Nitrile C₁₀H, CO CN ${\it Naphthoyl\ cyanide}$ [101°] Formed by heating (a)-naphthoylchloride with HgCl₂ at 100° Needles

(β) Naphthyl glyoxylic acid

C₁₀H, CO CO₂H [c 75°] Formed by gentle oxidation of (3)-naphthyl methyl ketone by dilute KMnO₄ (Claus a Tersteegen, J pr [2] 42, 518). Reduced by sodium amalgam to a oxy naphthylacetic acid C₁₀H, CH(OH) CO₂H

NAPHTHÝĽ-GUÀNIDINÉ C₁₁H₁₁N₈ 1 c O₈ Trimetric NH C(NH₂) NHC₁₀H₇ — B',H₂CO₃ crystals, a b c = 666 1 1 270 — B - B'HCl metric crystals (Haushofer, J 1882, 365)

Di (a) naphthyl-guanidine C21H1,Ns 26 NH C(NHC₁₀H₁), Menaphthylamine [c 200°] Formed by the action of gaseous cyanogen chloride on (a)-naphthylamine (Perkin, C J 9, 8, A 98,238) Small white needles with bitter taste, nearly insol water, sl sol alcohol and ether. Cyanogen passed into its ethereal solution forms $C_{22}H_{17}N_3$, a pale yellow crystalline mass, insol. water, m sol alcohol and ether, decomposed by cold HClAq in $C_{22}H_{12}N_3O_2$ erystallising in yellow scales [245°], and decomposed by acids into oxalic acid and di-naphthylguanidine —B'HCl amorphous, v sol alcohol

and ether, sl sol water -B'2H2PtCl8

Tri-(a) naphthyl guanidine C₃₁H₂₃N₃ 2 e Formed from C10H,N C(NHC10H,)2 [178°] (a) naphthylamine and MeS C(NC, H,)(NHC, H, [174°] (Evers, B 21, 962) Flat needles, insol water, v sol alcohol

(B) NAPHTHYL-GUANIDO BENZOIC ACID C18H15N2O2 26 C16H, NH C(NH) NH C4H4CO2H Formed by heating cyancarbimidamido-benzoic acid with excess of (B) naphthylamine (Griess, B 16, 338) Small crystalline spherules, insolether, v sl sol hot water and hot alcohol—
HA'HCl sparingly soluble six sided plates.

(a) NAPHTHYL-HYDRAZINE O, H, N, t.e.

(203° at 20 mm) C₁₀H,NH NH₂. [116°] Formed by making a paste of (a) naphthylamine and HClAq, adding NaNO, in the cold, filtering, and reducing with SnCl, the yield being 66 p c (Fischer, A 232, 236) Plates, al sol water, (Fischer, A 232, 236) v sol other solvents — B'HCl plates -B'2H2SO4 plates

Reactions -1 Acetone forms C, H, N, H CMe, [74°] -2 Pyruvic acid produces the acid C₁₀H,N H CMe CO₂H [159°], which forms the ether LtA' [100°] (Schlieper, A 239, 231) Di bromo pyruvic acid forms the acid C₁₀H,N₂H CH C(N₂HC₁₀H₁)CO₂H [196°] (Nast vogel, A 248, 89) -4 Aceto acetic ether forms oxy - naphthyl - methyl pyrazole C14H12N2O [c 190°] (knorr, B 17, 551)

Tetrahydride C.H. CH CH CH Obtained by treating a solution of the tetrahydride of (a) naphthylamine hydrochloride (18 g) with an equivalent quantity of NaNO, and dropping the mixture into a solution of SnCl₂ (45 g) dissolved in HClAq at 0° (Bamberger a Bordt, B 22, 630) Prisms (from boiling ligroin), sl sol water Reduces Fehling's solution at 30°-40° K₂Cr₂O, sets free nitrogen in the cold —*B'HCl

silvery plates, v sol water
(β) Naphthyl hydrazine C₁₀H₁₀N₂ s ε C₁₀H₇NH NH₂ [124°] Formed in the same way as its (a) isomeride (Fischer, A 232, 242) Plates, m sol water, v sol hot alcohol Turns red in air Its solution in cone HOAc is ppd

by water

Reactions -1 Acetone forms C10H, N2H CMe2 [65°] (Schlieper, A 236, 174) -2 Aldehyde yields C₁₀H,N₂H CH CH, [128°] -3 Phenylacetic aldehyde forms a crystalline hydrazide decomposing at 100° (Ince, A 253, 40) -4 Ace tophenone forms a hydrazide crystallising in to which at 175° forms the anhydride $C_{10}H_1N < N_{CO\ CH_2}^{N\ CMe} > CH_2 [119°]$ (Steche, A 242,

-6 Pyruvic acid in alcoholic solution yields C₁₀H₇N₂H ČMe CO₂H [166°], which yields the ether ÉtA' [131°] (Schlieper, A 236, 176) -7 Dr-bromo pyruvic acid yields yellow needles of CleH,N2H CH CO C(OH) N2HCleH,? insoluble in alkalis (Nastvogel, A 248, 85)—8 Aceto-acetic ether forms C₁₄H₁₂N₂O [190° Salts — B'HCl need

needles or plates .-*B',H,SO, . plates, sl. sol hot water -- Nitrate

very soluble needles.

(β) Naphthyl-throcarbasate

C.,H.N.H.HS CS N.H.C.,H., [145°]. Plates.

Acetyl derivative C.,H.NH NHAc. [165°]
(Hauff, A 253, 25), [167°] (Hillringhaus, B 22, 2657)
Formed from (\$) naphthyl-hydraxine and HOAc or Ac₂O Needles (from alcohol), m. sol hot water Reduces Fehling's solution

derivative C, H, NH NHBz Benzoyl[155°] Needles, insol water, v sol hot alcohol Di-bensoyl derivative CuH, N, HBz,

[163°]

D1-(a)-naphthyl-hydrasine C10H7.N2H2.C10H7

Hydraso naphthalene [275°]
Preparation—1 pt of azonaphthalene is finely suspended in a solution of 1½ pts of NaOH in 160–170 pts of alcohol, and the boiling mixture is treated with zinc dust till decolourised, it is then poured into water containing NH,HS and the pp is dried and extracted with benzene, from which it crystallises on cooling

Properties - Colourless plates Sublimable V sol alcohol, ether, and benzene, insol water By warming with HCl it is converted into a mixture of two isomeric di-amido-dinaphthyls (Nietzki a. Goll, B 18, 3253)

(1,4) - NAPHTHYL - HÝDRAZINE PHONIC ACID [14] C10He(N2H2) SO2H Formed by reducing the diazo-compound of naphthionic acid with stannous chloride (Erdmann, A 247, Tufts of white needles, sl. sol hot water, m sol hot HClAq -A'Na 4aq plates, al sol cold water

(1,4') Naphthyl-hydrazine sulphonic acid [14'] C₁₀H₆(N₂H₃)SO₃H Formed by reducing the diazo compound of the (1,4') naphthylamine sulphonic acid with SnCl₂ Plates, m sol water, v sol HCl -A'Na 3 aq needles, sl. sol.

Peru-Naphthyl-hydrazine sulphonic acid [11'] C10H6(N2H3) SO3H Formed, in like manner, from (1,1')-naphthylamine sulphonic acid Small plates, al sol hot water -A'K needles. v sol hot water —A'Na plates, v sl. sol water

(a) NAPHTHYL IMIDO-DIACETIC C₁₀H,N(CH₂CO₂H)₂ [133°] Formed by the action of chloro-acetic acid and Na₂CO₃ on (a)naphthyl amido acetic acid (Bischoff, B Colourless crystals, v sol alcohol

(a) Naphthylamids C₁₀H,N(CH₂CO₂H)(CH₂CONHC₁₆H₇) [199°]

Crystals (from benzene alcohol) Di-(a)-naphthylamide

[202°] C₁₀H,N(CH₂ CONHC₁₀H₇)₂ Crystals,

al sol ligroin

(β)-Naphthyl-ımıdo-diacetic acıd C, H, NO [182°] Formed by heating chloro-acetic acid (B) - naphthyl - amido - acetic acid with Na CO, Aq at 160° (B) Crystals, sol alcohol, sl The solutions have a sol ether, insol benzene bluish violet fluorescence

(α) - NAPHTHYL - β - IMIDO - BENZYL - MA-LONIC ETHER C., H., NO. s.e

C_aH_a C(NC₁₀H₇) CH(CO₂Et)₂. [145°] Formed by the action of w chloro-benzylidene (a)-naphthylamine upon sodio-malonic ether Crystal-line solid Sl sol ether By dilute HCl at 120° it is split up into acetophenone and (a)-naphthylamine (Just, B 19, 987

(β)-Naphthyl-β-imido-benzyl-malonic ether C.H. C(NC,H.).CH(CO,Et). H_NO. 1.6.

[140°]. Formed by the action of w-chlorobenzylidene-(B)-naphthylamineCieH,.N COl CeH, upon sodio malonic ether. Crystalline solid Sl sol ether By dilute HOl at 120° it is split up

into acetophenone and (β)-naphthylamine (Just)
(β)-NAPHTHYL-β IMIDO-BUTYRIC ACID CH₂ C(NC₁₀H₇) CH₂.CO₂H [92°] Needles, sol water Formed, together with its naphthalide, by heating a mixture of acetoacetic ether and (8) naphthylamine at 150°-180° By boiling with HCl it is converted into (Py 1 3) oxy methyl (\$)-naphthoquinoline

Naphthalide O24H20NO [200°] Needles, nearly insoluble in most solvents (Knorr, B 17,

DI - NAPHTHYL - IMIDO - THIOCARBAMIC ETHERS C10H7NH C(NC10H7) SR D1-naphthylalkyl \u2214 throureas Formed by heating di naphthyl thio-ureas with alkyl iodides (Evers, B 21,

Di-(a)-naphthyl-imido-thiocarbamic Methylether CioH, NH C(NCioH) SMe [136°] Plates, sol hot, v sl sol cold, alcohol Gives off HSMe on heating, leaving di-(a) naphthylcyanamide, which on boiling with dilute HClAq yields di-(a)-naphthyl-urea. Boiling alcoholic potash also converts it into di-(a)-naphthyl-urea potasi also converts i mo direja-naphyl-urez and HSMe Dilute H₂SO₄ at 160° forms (a)-naphthylamine and O₁₀H₂NH CO SMe —B'HI [174°] —B'₂H₂PtCl₂ [202°] Yellow powder Ethyl ether Eth' [98°] Prisms, al sol hot alcohol —B'HI [157°] —B'₂H₂PtCl₂ Propyl ether Prh' [95°] Plates — Prh [07°] —B'₂H PrCl

B'HI [97°] — B',H,PtCl_s

Ethylene derivative C₂H₁₈N₁S is.

C',H,N C SOH, CH

SOH, CH boiling di-(a)-naphthyl thio ures with ethylene bromide Needles, v sol alcohol —B',H,PtCl,

Di-(β)-naphthyl-imido thiocarbamic acid · Methyl ether C10H,NH C(NC10H) SMe [110°] Needles, v. e sol warm alcohol and etner -B',H,PtCl,

Ethyl ether EtA' [106°] —B',H,PtCl,

[155°]

Propyl ether PrA' [66°].-B',H,PtCl, [120°]

Ethylene derivative

 $C_{10}H_1N$ $C < N(C_{10}H_1)$ [172°]. Plates (from alcohol) $-B'_1H_1PtCl_0$ [146°] DINAPHTHYLINE v DI-AMIDO-DINAPHTHYL [172°]. Plates (from

(αβ) DI-NAPHTHYL-KETONE O, H, O ι ε .H.).CO Mol w 268 [135] S (alcohol) (C₁₀H₇)₂CO Mol w 268 [135°] S (alcohol) 13 at 14° Formed by heating (a) naphthoic acid with naphthalene and P_2O_3 at 210° (Kollarits a Merz, B 6, 544), by the action of a strip of zinc on a mixture of (a)-naphthoyl chloride and naphthalene (Grucarevic a Merz, B. 6, 1241), and by heating (3)-naphthoyl chloride with mercuric dinaphthyl at 175° (G a M) Pointed needles (from boiling alcohol) On distillation with soda lime it yields naphthalene and a mixture of (a) and (B) naphthoic acids

($\beta\beta$) Di-naphthyl ketone ($C_{10}H_{7}$)₂CO Obtained in two isomeric forms [125 5°] and [164°] by heating (β) naphthoic acid with naphthalene and P_2O_3 (K a M), or (β)-naphthoyl chloride with naphthalene and zinc (G a M) The two varieties may be separated by crystallisation

from ether chloroform Both varieties yield naphthalene and (β) naphthoic acid on distillation with soda lime The solubility of the variety melting at 164° in alcohol at 19° is less (08) than that of the variety melting at 1255° The latter variety may also be prepared by distilling calcium (β) naphthoate (Hausamann, B 9, 1515)

Di-naphthyl ketone (C₁₀H₁)₂CO Formed by distilling potassium naphthalene (3) sulphonate with KHC₂O₄ (Giuseppe, B 6, 546)

NAPHTHYL-MELAMINE v CYANIC ACIDS

(a) NAPHTHYL MERCAPTAN C, H,S 2 e C₁₀H, SH Thomaphthol Mol w 160 (285°) SG 2 11729, 23 11549 Formed by reducing naphthalene (a) sulphonic chloride with zincdust and diluté H₂SO₄ (Schertel, A 132, 91, Krafit a Schönherr, B 22, 822) Formed also by saponifying its ethyl ether which may be formed by the action of potassium xanthate on (a) diazonaphthalene chloride (Leuckart, J pr [2] 41, 216) Colourless oil, with unpleasant smell, sl sol aqueous alkalis, v sol alcohol Oxidised in alcoholic solution by and ether the air to di (a) naphthyl disulphide [91°] Yields di naphthyl sulphide [107°] on heating –

Hg(SC₁₀H₁)₂ —Pb(SC₁₀H₁)₂ yellow pp Ethyl ether C₁₀H₁SEt. (167.5°) at 15 mm S G ² 1 1198, ²² 1 0797 Formed from C₁₀H₁SH by heating with EtI, alcohol, and KOH at

120°-150°

Acetyl derivative C, H,SAc (188° at 15 mm) SG 1 1519

Benzoyl 'derivative CoH, SBz

(262° at 15 mm).
(8) Naphthyl mercaptan C, H, SH [75°].
(Billeter, B 8, 463, L), [81°] (K a S) (286°) [75°]. Formed by reducing naphthalene (B) sulphonic chloride, and also by heating (β) diazo-naph thalene chloride with a solution of EtO CS SK. saponifying the oily product, and boiling with zinc dust and HClAq (Maikopar, Z 1869, 711, Leuckart, J pr [2] 41, 220) Small plates (from ether), sl sol water Not volatile with steam Yields the corresponding disulphide on oxida tion —Pb(SC₁₀H₁)₂ orange powder Ethyl ether C₁₀H₁SEt [16°]

15 mm)

Acetyl derivative C10H,SAc [53 5°] (191° at 15 mm) Formed by heating the mercaptan with AcCl at 75°

Benzoyl derivative C, H, SBz (267° at 15 mm)

DI (a)-NAPHTHYL METHANE C21H1 $(O_{10}H_7)_2OH_2$ [109°] (above 360°) S (alcohol) 8 in the cold, 6 6 at 78° Formed by the action of H₂SO₄ on a cooled mixture of naphthalene (5 pts.), methylal (1 pt.) and chloroform (20 pts.) (Grabowski, B. 7, 1605) Short prisms (from alcohol), v. sol. ether and chloroform. Not affected by chromic acid mixture Picric acid compound C21H162C6H2(NO2)3OH Reddish yellow prisms (from chloroform)

Di (\$\beta\$-naphthyl-methane [92°] Prepared by reducing di (\$\beta\$) naphthyl-ketone with \$\beta\$ and HIAq (Richter, \$B\$. 13, 1728) Slender white needles, \$\beta\$ sol alcohol and benzene Yields C_nH₁₄Br₂ [164°] and C₂₁H₁₄Br₄ [150°-160°]

NAPHTHYL-METHYL-ALCOHOL v. NAPH THYL CARBINOL.

(a) NAPHTHYL METHYL-AMINE

O₁₀H,NHMe Methyl (a)-naphthylamine (298° uncor) Formed, together with dinaphthylamine, by passing McCl into melted (a) naphthylamine (Landshoff, B 11, 688) Dark red oil Its alcoholic solution gives a violet pp with FeCl₂ -B'₂H₂PtCl₂ 2aq

Acetyl derivative C, H, NMeAc (L), [95°] (Norton a Livermore, B 20, 2272) Small white prisms, sl sol water, v sol alcohol and ether Dilute nitric acid (10 pc) forms

 $C_{10}H_{4}(NO_{2})$ NMeNO₂ [157 5°]

Bensoyl derivative CioH, NMeBz [121°]

Formed by heating (a) naphthyl-di-methylamine with BzCl at 180° (Hess, B 18, 687) Crystals (a)-Naphthyl-di-methyl-amine C₁₂H₁₃N is C₁₀H,NMe₂ (267°) (L), (274 5° 1 V at 711 mm) (Bamberger a Helwig, B 22, 1815) S G ²⁰ 1 0423 Formed by heating (a) naphthylamine (1 mol) with MeI (2 mols) and MeOH (Landshoff, B 11, 643, J pr [2] 17, 286, Monnet, Reverdin, a Nolting, B 12, 2305) Prepared by heating (a)-naphthylamine hydrochloride with MeOH for 8 hours at 170° (Hantzsch, B 13,

1348, Friedlander, B 21, 3124) Oil
Reactions -1 Forms a nitroso-compound which decomposes in an acid aqueous solution into (1, 4) nitroso naphthol and dimethylamine 2 Nitric acid forms two nitro derivatives [88°] and [128°] — 3 By condensation with benzoic aldehyde in presence of ZnCl, at 110° it yields C.H. OH(Cl.-H.NMe.), [188°] — 4 C.H.NMe, CHO[14] yields, in like manner. NMe₂ C.H. CH(C₁₀H₈NMe₃)₂ [179²] —5 COCl₂, followed by Aq, yields NMe, C₁₀H₆ CO₂H [164²] Platinochloride B'₂H₂PtCl₆ yellow

Methylo-10dide B'MeI Yellowish green flat needles, decomposed at 164° uncor Not affected by NaOH, but Ag2O yields a strongly alkaline hydroxide - (B'MeCl)2PtCl4

C_eH_e< ar Tetrahydride (262°) at 721 mm Formed by reducing the base, dissolved in isoamyl alcohol, with sodium (B a H) Colourless oil Yields a colouring matter with p diazobenzene sulphonic acid Reduces AgNO₂ Oxidised to adipic acid by KMnO₄ Yields B'₂H_.PtCl₆ and B'MeI [164 5°] KMnO₄ Yields B'₂H₂PtCl₆ and (β)-Naphthyl-methyl-amine

BensoyldersvatsveCieH, NMeBz [169°], glistening plates Formed by heating di methyl-(8)-naphthylamine with benzoyl chloride at 180°

(Hess, B 18, 688)

(β) Naphthyl-di-methyl-amine C, H, NMe, [46°] (305° cor) Formed by heating commercial trimethylamine with (β)-naphthol at 200° (Hantzsch, B 13, 2055), and by heating (8) naphthylamine with MeI and NaOHAq at 120° (Bamberger a Müller, B 22, 1306) Forms very soluble salts --B'_2H_PtCl_s

Methylo-sodide CloH, NMe_I. Tables, sl

With Ago it yields a strongly sol cold water

alkalıne hydroxide

ar-Tetrahydride C.H. CH CNMe.

(287°) at 715 mm Formed by reducing C₁₆H, NMe₂I dissolved in isoamyl alcohol with sodium (Bamberger a Müller, B 22, 1806) Colourless oil. Reduces auric chloride and AgNO, FeCl, gives a turbidity and a yellow

colour K2Cr2O, and H2SO4 give a yellow pp and, on heating, a dirty-green colour KMnO. oxidises it to adipic acid —B'HCl —B',H,PtCl,—B'HClHgCl. [127 5°] Needles, v sl sol. cold, v sol hot water Picrate needles

ac-Tetrahydride C.H. CH2 CH2 CH2 CH2

(166 5° at 22 mm) Formed at the same time as the aromatic isomeride —B'HCl needles, v sol water -B'2H2PtCl orange needles, v sol water

D1 (β) naphthyl methyl-amine ($C_{10}H_{1}$)₂NMe [140°] Formed from ($C_{10}H_{1}$)₂NH and MeI at 100° (Ris, B 20, 2619) Needles, m sol cold 100° (Ris, B 20, 2619) alcohol, msol ligroin

Isomeride of naphthyl methyl-amine v NAPHTHYL-CARBINYL AMINE

(a) NAPHTHYL METHYL KETONE C12H10O te CloH, CO CH, [34°] (297°) Formed by the action of AcCl in presence of AlCl, on naphthalene dissolved in ligroin (Pampel a Schmidt, B 19, 2898, Claus a Feist, B 19, 3180, J pr[2] 42, 517) Crystals, insol water, v sol alcohol and ether Oxidised by KMnO, to (a) naphthyl glyoxylic acid Yellow ammonium sulphide at

220° forms $C_{10}H$, CMe $<_{NH}^{Q}$ [154°] (Willgerodt,

B 20, 2468)

Oxim C₁₀H, CMe(NOH) [101°] (P a. S), [145°] (C a F)

Phenyl hydraside C,H, CMe(N,HPh)
[146°] (P a S), [173°] (C a F) Needles
Anvide C,H, CMe(NPh) [130°] It will be seen that the melting points of the oxim and phenyl hydrazide of the ketone prepared by Claus are the same as those of the like derivatives of

(β) Naphthyl methyl ketone C₁₀H, CO CH, [52°] (301°) Formed together methyl contract to the contract of the contract together methyl contract t (301°) Formed, together with the (a)isomeride by the action of Ac.O on naphthalene in presence of AlCl, (Roux, A Ch. [6] 12, 289, Müller a Von Pechmann, B 22, 2561) Leaflets, nearly insol cold water Oxidised by dilute KMnO, to (β) naphthyl glyoxylic acid [c 75°], further oxidation forms (8) naphthoic acid Sodium amalgam reduces it to C10H, CH(OH) CO2H [176°]

Oxem C₁₀H, C(NOH) CH, [145°] Acetyl derivative of the oxim [134°] Phonyl-hydraside [171°]

NAPHTHYL METHYL OXIDE v Methyl ether of Naphthol.

(a) NAPHTHYL - DI - METHYL - PYRROLE

 $C_{10}H_{15}N \text{ s.e. } C_{10}H_{7}N \begin{matrix} \text{CMe CH} \\ \text{CMe CH} \end{matrix}$ [123°] (312°) Formed by heating its dicarboxylic acid at 250° (Knorr, A 236, 309) Insol water, v sol alcohol, ether, and chloroform

(β) Naphthyl-di methyl-pyrrole (841°) Formed in like manner

(a)-NAPHTHYL - DI METHYL PYRROLE DICARBOXYLIC ACID C, H, NO, 4 e

CMe C CO.H CMe C CO.H [244°] Formed by sa ponifying its ether, which is obtained by the action of (a)-naphthylamine on diacetyl succinio ether (Knorr, A 236, 808) Needles — K.A".—
BaA" — AgHA".

Ethylether Et.A". [91°].

(8)-Naphthyl-di-methyl pyrrole-di-carboxylic CMe C CO2H acid C10H7Ne Its di ethyl ether √CMe Ċ CO.H

is obtained by mixing acetic acid solutions of di aceto succinio ether and (8)-naphthylamine (Knorr, B 18, 304) Sparingly soluble in most Begins to decompose at 260° with solvents

bevolution of CO₂—BaA"—BaH₂A"₂

Dt-ethyl ether A"Et₂ [124°], needles

DI-NAPHTHYL METHYL- THIOUREA v Methyl ether of DI NAPHTHYL-IMIDO THIOCARBAMIC

DI-(a)-NAPHTHYL OXIDE (C, H,),O Naphthylether [110°] Formed by heating (a) naphthol with ZnCl, or HCl (Merz a Weith, B 14, 195) Plates or tables, sol hot alcohol and ether May be distilled unchanged —Picrate

C₂₆H₁₄O₂C₆H₂(NO₂)₃(OH) [115°] Red crystals Di-(β)-naphthyl oxide (C₁₆H₁)₂O [105°] Obtained by boiling (3) naphthol with dilute (50 pc) H₂SO₄(Graebe, B 13, 1849), or by heating it with ZnCl₂ (2 pts) at 190°, or with gaseous HCl (M a W) Formed also by distilling aluminum (B)-naphthol (Gladstone a Tribe, C J 41, 15) Pearly plates (from alcohol), sol ether Gives an orange colour with conc H.SO.

Picrate C20H14O2C6H2(NO2)3OH [122°]

Small orange prisms
DI-(a) NAPHTHYL-PARABANIC ACID $C_{2s}H_{14}N_2O_2$ so $CO < N(C_{10}H_7)CO > N(C_{10}H$ [246°]

Formed by passing cyanogen gas into an alcoholic solution of methyl di (a)-naphthyl-imido-thio-carbamate and heating the crystals that separate with alcoholic HCl (Evers, B 21, 973) Needles, v sol hot alcohol, sl sol ether, insol water and dilute acids Decomposed by boiling alcoholic potash into CO2, oxalic acid, and (a) naphthylamine

(a)-NAPHTHYL PHENYL-AMIDO METHYL KETONE C18H15NO to C10H, CO CH2 NHC6H5 Formed by the action of aniline on C₁₀H, CO CH, Br in alcoholic solution (Pampel a Schmidt, B 19, 2899) Red crystals

NAPHTHYL-PHENYLcompounds

PHENYL-NAPHTHYL COMPOUNDS

(a) NAPHTHYL DI PHENYL METHYLENE. ANTINE C₂₃H₁₇N t & C₁₀H, N CPh₂ Formed from (a)-naphthylamine and benzophenone chloride Ph₂CCl₂ (Pauly, A 187, 215) Golden plates (from ether), split up by soids into benzophenone and (a)-naphthylamine

TRI-(a)-NAPHTHYL PHOSPHATE (C₁₀H₂O)₃PO [145°] Prepared by he (C₁₀H₂O)₂PO [145°] Prepared by heating (a)-naphthol with POCl₂, the yield being 65 p c of the theoretical (Schäffer, A 152, 289, Heim, B. 16, 1769) Small glistening needles

Tri · (β) - naphthyl - phosphate (C₁₀H₂O)₂PO 1°] Prepared by heating a mixture of (β)naphthol and phosphorus oxy-chloride, the yield being 65 p c of the theoretical (Heim, B 16, 1768, cf Schaffer) Fine white needles Insol water, sl sol cold alcohol

NAPHTHYL PHOSPHOROUS ACID v NAPH-

THALENE PHOSPHINIC ACID

β-(a)-NAPHTHYL-PROPIONIC ACID C,H,2O, 10 C₁₀H, CH₂ CH₂ CO₂H Formed by reducing naphthyl-acrylic acid with sodium amalgam (Brandis, B 22, 2156). Needles (from alcohol), sol. boiling water.

(a) NAPHTHYL PROPYLENE ↓ THIO UREA

CH, CHS SC NH C,0H, [184°] Formed by heating s naphthyl allyl thio urea [145°] with HClAq at 100° (Prager, B 22, 3001) Tables, v sol chloroform, m sol ether, insol water – B'₂H₂PtCl₆ [206°] —B'C₆H₂(NO₂)₅OH [192°]

NAPHTHYL PURPURIC ACID C11H7N3O4 The K salt is formed by the action of aqueous KCy on di nitro naphthol (Sommaruga, B 4, 94, The free acid is unstable The A 157, 328) K salt is golden brown with metallic lustre Potash fusion yields benzoic, phthalic, and hemi mellitic acids The following salts were dried at 100° NH₄A' —KA' —CaA' ₂—BaA' ₂

DI-(a)-NAPHTHYL PYRAZINE TETRAHY

DRIDE C₁₀H₇N < CH₂ CH₂ CH₂ NC₁₀H₇ Dr-naph thyl-de ethylene diamine [265°] Formed from ethylene bromide, (a) naphthylamine, and NaOAc (Bischoff, B 22, 1782) Prisms, v sl sol al cohol

Dı (β) naphthyl-pyrasine tetrahydride [228°] Formed by the action of C.H.Br., on (B) - naphthylamine in presence of Na.CO, (Bischoff, B 23, 1984) Colourless crystals, insol water, alcohol, ether, and HClAq, sol hot HOAc

(a) NAPHTHYL - PYRIDINE HEXAHY **DRIDE** C₁₀H₇NC₅H₁₀ (185°-190° at 5-10 mm) Formed by heating piperidine (2 mols) with (a) bromo naphthalene (3 mols) for 10 hours at 255° (Lellmann a Buttner, B 23, 1383) Thick yellow oil, with faint fæcal odour, rapidly be coming brown V sol alcohol and ether A coming brown solution of its hydrochloride is ppd by HgCl2, by ZnCl, and by chloride of gold—B'HCl groups of needles, v sol water -B'2H2PtCl62aq

(β)-Naphthyl pyridine hexahydride Resembles the preceding in mode of preparation Colourless prisms, becoming and properties grey on keeping -B'HCl -B'aHaPtCl, 6aq

DINAPHTHYL-DIQUINONE, so-called. Ometion of the Contraction of th -0-

Obtained by oxidation of dinaphthyl-diquin hydrone $C_{20}H_{12}O_4$, a black powder formed by the action of dilute H_2SO_4 on (β) naphthoquinone (Stenhouse a Groves, C J 33, 415) Formed also by the oxidation of (\$)-amido (a) naphthol by FeCl, or CrO, (Zincke a Rathgen, B 19, 2483) Small orange prisms, insol water, v sl sol other solvents Not affected by boiling

HNO, or by H.80, Reactrons —1 Yields on reduction dinaphthyl dihydroquinone'-2 Distillation with sincdust converts it into dinaphthyl.—8 Alkalis form a green solution which, on exposure to air, changes to red from formation of O₂₀H₁₀(OH),O₄ [245°-250°] (Korn, B 17, 3020) $\stackrel{-}{-}$ 4 KMnO₄ oxidises it to diphthalylic acid $C_{16}H_{16}O_6$ 5 Anilms forms $O_4H_{\odot}N_{\bullet}O_2$ crystallising in red plates [250°] and forming a hydrochloride $O_{44}H_{\odot}N_{\bullet}O_2H_2Cl_2$ crystallising in needles

Iso-dinaphthyl-diquinone C₂₀H₁₀O₄ [250°-260°] Formed by oxidising di-(\$) naphthyl with CrO₂ in HOAc (Staub a Watson Smith, C J 47, 104) Amorphous yellow powder, sol. HOAc, al. sol. most liquids. Turns brown at 215°.

· NAPHTHYL - ROSINDULINE C.H., N. 60

C.H. < C(NC10H,) CH C NPh > C.H. [247°] Formed by heating benzene azo-di-(a)-naphthylamine with aniline and alcohol at 165° (Fischer a Hepp, A 256, 246) Black needles, forming a blue solution in conc H₂SO₄ Conc HClAq at 210° splits it up into (a)-naphthylamine and rosindone C₂₂H₁₄N₂O

(a) NAPHTHYL SILICATE C40H28S1O4 te (C₁₀H₇)₄SiO₄ (425°-430° at 180 mm) Needles (Hertkorn, B 18, 1696)

 (β) -Naphthyl silicate. (480° at 188 mm.) Crystalline (H)

NAPHTHYL-SULPHAMIC ACID V NAPHTHYL-AMINE V BULPHONIC ACID

NAPHTHYL SULPHATE.

Naphthyl sulphuric acid C, H, SO, H,O SO₂ OH Formed by the action of Cl SO, OH on a cold solution of (\$\beta\$) naphthol in CS, (Armstrong, \$B\$ 15, 204) It is also formed by dissolving (\$\beta\$) naphthol (1 pt) in cold H, SO, (2 pts) (Nietzki, B 15, 305) - NaA' Slender leaflets, v e sol water Ppd from aqueous solution by NaCl Split up by boiling HClAq into (β) naphthol and NaHSO. Does not react with diazo salts - KA' scales (from hot water) With PCl, it yields chloro naphthalene Bromine forms brome naphthel [84°]

DI-(a) NAPHTHYL SULPHIDE C.H. S 2 8

(C₁₀H₇)₂S [110°] (290° at 15 mm)

Formation —1 By distilling a dry mixture of potassium naphthalene (a) sulphonate and potassium sulphocyanide (Armstrong, B 7,407) 2 By distilling the lead salt of (a) naphthyl mercaptan under diminished pressure (Krafft a Schönherr, B 22, 823) -3 By heating (a) naphthyl mercaptan as long as H₂S is evolved (Leuckart, J pr [2] 41, 217)—4 By heating (C₁₀H₂S)₂Pb with (a) bromo naphthalene at 235°

for 4 hours (Krafft a Bougois, B 23, 3045)

Properties—Needles, v sol benzene and
HOAc, sl sol alcohol Chromic acid in HOAc oxidises it to the sulphoxide [165°], and finally

to the sulphone [187°] (Krafft, B 23, 2368) (αβ)-Di-naphthyl sulphide (C₁₀H₇)₂S [(290° at 15 mm) Formed by heating the lead salt of (\$\beta\$) naphthyl mercaptan with (\$\alpha\$) bromo naphthalene at 230° (Krafft, \$B\$ 23, 2368) Lus trous leaflets (from alcohol) Oxidised by CrO.

an HOAc to $(C_{10}H_{\gamma})_2SO$, [123°] Di (β) naphthyl sulphide $(C_{10}H_{\gamma})_4S$ [151°]. (296° at 15 mm) Formed by distilling the lead salt of (β) naphthyl mercaptan under 10 mm pressure (K a S) Plates, v sl sol hot alcohol, v sol CS₂ Oxidased by CrO₂ in HOAc to (C₁₀H₁)₂SO₂ [177°] (Krafft, B 28, 2366)
(aa) D1-naphthyl disulphide (O₁₆H₁)₂S₂. [91°]

Formed by oxidising (a) naphthyl mercaptan by exposing its alkaline solution to the air (Schertel, A 132, 91, Leuckart, J pr [2] 41,

Monoclinic crystals, sl sol alcohol Di.(6) naphthyl disulphide (0,0H,),S, [137°] (L), [139°] (O) The chief product obtained by saponification of the oil which is formed by the action of potassium xanthate on (β) diazonaphthalene chloride (Leuckart, J pr [2] 41, 221) Formed also by reducing naphthalene (β) -sulphonic chloride with HIAq (Cleve, β . 21, 1100). Colourless plates, msol. water, v. sol.

alcohol and ether Reduced by zinc and H2SO4

to (β) naphthyl mercaptan.

(β)-NAPHTHYL SÛLPHOCYANIDE C, H, NS e C₁₀H₁SCN [35°] Formed by the action of cyanogen chloride on Pb(SC₁₀H₁)₂ (Billeter, B 8, 463) Decomposes on distillation KHS forms KSCN and HSC₁₀H₁, Cone HClAq forms C₁₀H₁SH₂, NH₂, and CO₂ Sodium amalgam re-

C₁₀H, SH, NH₂, and CO₂ Sodium amalgam reduces it to sodium oyanide and (C₁₀H₁)₂S₂
(aa) DI-NAPHTHYL SULPHONE (C₁₀H₁)₂S₂
[187°] Formed by oxidising (aa)-di-naphthyl sulphide by CrO₂ in HOAc (Krafit, B 23, 2368,

cf Leuckart, J pr [2] 41, 218)
(αβ) Di naphthyl sulphon sulphone $(C_{10}H_7)_2SO_2$ [123°] Formed, together with the $(\beta\beta)$ isomer de by heating naphthalene (8 pts) with H₂SO₄ (8 pts) at 180° (8tenhouse a Groves, B 9, 682, Cleve, B 10, 1723, Bl [2] 25, 256, cf Berzelus, A Ch [2] 65, 290) Formed also by oxidising the corresponding di naphthyl sulphide (Krafft, B 23, 2369) Prisms (from CS2), m sol boiling alcohol and ether

(ββ) D1-naphthyl-sulphone $(C_{10}H_{\tau})_2SO_{z}$ Formed as above, and also by dissolving (ββ) di naphthyl sulphide (1 pt) in HOAc (200 pts), warming, slowly adding a mixture of $K_2Cr_2O_2$ (3 pts) dilute (1 3) H_2SO_2 (20 pts) and HOAc (50 pts), filtering, evaporating, and crys tallising from alcohol (Krafit, B 23, 2366) Long white needles When heated with PCl, it yields (B) chloro naphthalene and naphthalene (B) sulphonic chloride (Cleve, Bl [2] 25, 25)

DINAPHTHYL SULPHONIC ACID v DI NAPHTHYL

(αα) DI-NAPHTHYL SULPHOXIDE

(C₁₀H₁)₂SO [164 5°] Formed by oxidation of (aa) di naphthyl sulphide with chromic acid mixture and HOAc (Krafft, B 23, 2367) Formed also by oxidation of naphthylene di naphthyl sulphoxide C_{so}H₂₀SO [111°] (Ekstrand, B 17, 2603) White crystals (from alcohol)

NAPHTHYL SULPHURIC ACID v NAPHTHYL SULPHATE

NAPHTHYL SULPHYDRATE v NAPHTHYL MERCAPTAN

(a) NAPHTHYL-THIOCARBAMIC ACID

C, H NH CO SH Methyl ether MeA' [122° Formed by the action of dilute H2SO, on methyl di naphthyl imido thiocarbamate [136°] (Evers, B 21, 970) Needles, v sol dilute alcohol, insol Alcoholic amwater, alkalis, and dilute acids monia forms, on heating, (a) naphthyl-urea

Ethylene derivative

 $co <_{\rm S~CH_z~CH_z}^{\rm N(C_{10}H_z)} >$ [102°] Formed by the action of dilute HClAq at 200° upon the substance $C_{10}H_1N$ $C < N(C_{10}H_1) > (Evers, B 21, CH_2OH_2)$ 970) Needles

(B) Naphthyl-thiocarbamic acid ether C. H.NH CS OEt [97°] Formed by heating (8) naphthyl thioarbimde with alcohol at 180° (Cosner, B 14, 58) Needles or plates, v e sol chloroform, m sol alcohol and ether — C,-H,NAg CS OEt Ppd by adding ammoniacal AgNO, to the alcoholic solution

(a)-Naphthyl-dithiocarbamic acid

Methyl ether C.H.NH.CS SMe [185°], Formed by heating O.H.NH CO SMe with CS. (E.). Small needles, m sol. hot dilute alcohol.

Ethylene derivative OS < N(C, H,) CH, CH, Formed by the action of CS, on $CO < N(C_{10}H_{1})$ at 160° (Evers, B 21, 972).

Pearly plates (from hot alcohol)

(8) Naphthyl-dithiocarbamic acid Tetrahydrede. Tetrahydronaphthylamine salt $C_{10}H_{11}NH_2S$ CS $NHC_{10}H_{11}$ [1422] Formed from the tetrahydride of (β) naphthylamine and an ethereal solution of CS, (Bamberger a Muller, B 21, 857) Needles

(β)-NAPHTHYL-THIO-SEMI-CARBAZIDE C₁₀H,NH NH CS NH₂ [204°] Formed by heat ing (β)-naphthyl hydrazine hydrochloride with ammonium sulphocyanide in alcoholic solution (Hauff, A. 253, 30, Hillringhaus, B 22, 2657)

Crystals, insol water, al sol cold alcohol
(a)-NAPHTHYL-THIOCARBIMIDE
C1-H-N CS Naphthyl mustard oil [58°] Formed from di-naphthyl-thio urea by distilling with P_2O_3 (Hall, P M [4] 17, 304) or by heating it with HClAq (84 pc) at 150° (Mannger, B 15, 1414) Formed also by heating di naphthylcyanamide with CS, at 200° (Huhn, B 19, 2406) Long white needles, sol alcohol, ether, and benzene With naphthylamine in alcoholic solu tion it combines, forming di naphthyl thio-urea Aniline forms phenyl naphthyl thio urea

(β) Naphthyl thiocarbimide C, H, NCS [62°] Obtained in the same manner as its (a) isomeride (Cosiner, B 14, 61, Huhn, B 19, 2407) Needles

(β)-NAPHTHYL-THIOCARBIZINE C,,H,NS $_{\circ}$ e $C_{1\circ}H$, $N<_{CS}^{NH}$. [254°] Formed by heating (8)-naphthyl thio-semi-carbazide with (20 pc) H₂SO₄ at 135° (Hauff, A 253, 31) Pearly plates, insol water, sl sol ether, v sol warm alcohol May be sublimed -B'HCl 'v sol hot water -B'H2PtCl, -B'HNO

DI-(a)-NAPHTHYL-THIOHYDANTOIN $C_{10}H_{7}N \subset <_{8CH_{2}}^{N(C_{10}H_{7})}>CO$ C.H., N.SO [176°]. Formed by the action of chloro-acetic acid on di-(a) naphthyl thio-urea (Evers, B 21, 974) Plates, insol. water, v sol alcohol

D: (β) -naphthyl-thiohydantoin [174°] sembles the (a) isomeride in mode of preparation and properties

NAPHTHYL-THIOSINAMINE 18 NAPHTHYL-ALLYL-THIO UREA $(q \ v)$

(a) NAPHTHYL-THIO-UREA C,H,aN,S te. C₁₆H₇NH CS NH₂ [198°] Formed by heating naphthylamine hydrochloride with ammonium sulphocyanide (De Clermont a Wehrlin, C R. 82,512) Small trimetric prisms (from alcohol); sl sol. water, ether, and cold alcohol

Acetyl derivative C₁₀H,NH CS NHAc [198°]. S (alcohol) 25 at 78° Formed from (a)-naphthylamine and acetyl sulphocyanide (Miquel, Bl [2] 28, 108) Slender needles

Benzoyl derivative C₁₆H,NH CS NHBz. [173°] S (alcohol) 2 at 78° Formed from (a)-naphthylamine and benzoyl sulphocyanide (Miquel, A Ch [5] 11,826) Lus prisms (from alcohol), insol ether Lustrous yellow

(β) - Naphthyl - thio - ures C₁₀H,NH.OS NH... [180°] Formed by heating (β)-naphthylamine hydrochloride with potassium sulphocyanide (Cosiner, B. 14, 61). White trimetric plates.

Di - (a) - naphthyl - thio - urea C. H. N.S i.s. CS(NHC, H,), [207° cor] (E), [197°] Brieger, B. 12, 1860, Huhn, B 19, 2405) Formed by heating (a) naphthylamine (100 g) with CS, (50 g) and alcohol (500 g) for 14 hours at 75° (Delbos, 4 64, 371, Evers, B 21, 963) Formed also by passing H_2S into a boiling solution of dinaphthyl-oyanamide $(C_{10}H,N)_2C$ in dry benzene Needles, almost insol alcohol, ether, and benzene, sol introbenzene By adding HgO to its boiling solution in dry benzene it is re converted into C(NC₁₀H₇)₂. MeI at 100° forms methyl di - naphthyl - imido - thio - carbamate C₁₀H,N C(NHC₁₀H₇)SMe [136°] (v DI NAPHTHYL-IMIDO THIO CARBAMIC ETHERS

Octohydrids CS(NHC10H11)2. [170°] Formed by heating (a) naphthylamine tetrahydride with CS2 and alcohol as long as H2S is given off (Bamberger, B 21, 1795) sol alcohol, m sol ether

Di (β) naphthyl-thio-urea $CS(NHC_{10}H)_2$ [193°] (C, H), [203° cor] (E) Prepared by heating (3) naphthylamine in alcoholic solution with CS, for 14 hours at 75° (Cosiner, B 14, 61, Evers, \hat{B} 21, 963) Formed also by passing H.S into a boiling solution of s di (3) naphthylcyanamide (carbo di (3) naphthyl imide) in dry cumene (Huhn, B 19, 2407) White plates (from hot introbenzene), v sl sol alcohol and ether With MeI it forms the compound C₁₀H,NH C(NC₁₀H,) CSMe [110°], v DI NAPH-THYL-IMIDO THIO CARBAMIC ACID By adding HgO to its boiling solution in benzene it is converted into $C(NC_{10}H_{*})_{2}$. When heated with alcoholic NH₂ at 100° it yields (β) naphthylamine and (β) naphthyl-thic ures (Gebhardt, B 17, 3045) With mercuric cyanide and ammonia it yields CN C(NC₁₀H₁) NHC₁₀H₁, [166°], which forms an acetyl derivative [141°] and a benzoyl derivative

[188°] (Hefelmann, C C 1885, 884)

Octohydride CS(NHC₁₀H₁₁), [166°]

Formed by boiling with alcohol the product ob tained by the action of CS, on the tetrahydride of (β)-naphthylamine (Bamberger a Müller, B 21, 858) White needles, v sol alcohol, v e sol

ether and benzene

NAPHTHYL-TOLYL-AMINE v TOLYL NAPH THYL AMINE

(a) NAPHTHYL UREA C₁₁H₁₀N₂O te C₁₆H₂NH CO NH₂. Obtained by saturating a so lution of (a)-naphthylamine in dry ether with cyanic acid gas, and crystallising from hot alco hol (Schiff, A 101, 90) Formed also, together with di naphthyl urea, by heating naphthyl amine hydrochloride (3 pts) with urea (1 pt) at 150°-170° (Pagliani, G 9, 30) Flat needles, nearly insol water, m sol alcohol, v sol ether Decomposes at 250° without previous fusion

(β)-Naphthyl-urea C₁₀H,NH CO NH₂ 287°] Prepared by heating urea with (8)-naphthylamine hydrochloride (Cosiner, B 14, 62) White needles, sol hot alcohol and hot water

Di-(a) naphthyl-ures CO(NHC₁₀H₇)₂ [270°]. Formation—1 By heating the acid exalate of (a)-naphthylamine (Delbos, A Ch [4] 21, 68), di-naphthyl-oxamide being first formed (Zinin, A 108, 228) -2 By gradually heating (a) naphthylamine (2 pts) with urea (1 pt) to 120° (Pagliani, G 9, 28) —8 By boiling di-(a) naphthyleyanamide with dilute alcohol (Huhn, B. 19, 2405) --4 By heating (a)-naphthylamine with carbamic ether at 185° (Smolka, M 11, 200)

Properties -Plates or needles, insol water, si sol boiling alcohol Yields naphthylamine and no NH, on decomposition by KOH

s-D₁- (β) -naphthyl-urea CO(NHC₁₀H₇)₂ [293°]

(H), [286°] (E)

Formation -1 By the action of HgO on di (β) naphthyl thio-urea suspended in spirit (Huhn, B 19, 2406) -2 By boiling di (β) naphthyl cyanamide $C(NC_{10}H_{\tau})_2$ with dilute alcohol (H.) -3 By boiling potassium di (β) naphthoyl-hy droxylamine with water (Ekstrand, B 20, 1360)

Properties - Slender needles, sl sol alcohol,

ether, benzene, and nitrobenzene

u D₁-(β) naphthyl urea C, H,),N CO NH, [193] Formed by heating the chloro-formyl derivative of di (3)-naphthylamine with ammo nia for an hour at 140° (Kym, B 23, 428) Groups of long needles (from alcohol), al sol cold alcohol)

(N(C₁₀H₁)₂)₂CO Formed by heat Tetra (β) naphthyl-urea [288°] (K a L), [295°] (K) Formed by heat ing di (8) naphthylamine with (O₁₀H₁)₂N COCl at 200°-260° (Kuhn a Landau, B 23, 811, 2161, Kym, B 23, 1542) Prismatic needles, sl. sol alcohol and ether, v sol hot benzene

NAPHTHYL-UBETHANE v NAPHTHYL-CARB-AMIC ETHER

NARCEINE C₂H₂NO₂. [134°] (Blyth), [145° cor] (Hesse, A 129, 251), [162°] (Claus a Meixner, J pr [2] 87, 1, cf Dott, Ph [3] 20, 3.35) S 08 at 13° S (80 pc alcohol) 1 Occurs in opium (Pelletier, A Ch [2] 50, 262, Cauchi A Ch [3] 50, 262,

Couerbe, A Ch [2] 59, 151)

Preparation —1 The aqueous extract of opium, from which morphine has been separated by Gregory's process, is mixed with ammonia, fil tered, and ppd by lead acetate The filtrate is freed from lead by H₂SO₄, neutralised by ammonia, and evaporated The narceine is recrys tallised from water (Anderson, Tr E 20, iii 347) -2 A solution of the opium bases in HClAq is mixed with excess of NaOAc and allowed to stand for 24 hours The filtrate evaporated to a small bulk on the water-bath deposits, after 24 hours, pure narceine (Plugge, Ar. Ph [8] 25, 343)

Properties - Silky needles (containing 2aq), v. sol hot water and alcohol, sl sold cold water and chloroform, insol ether Cannot be sublimed It loses its water of crystallisation at 100°, and at 140° gives off another H₂O (Hesse, B 7,105) It is insol cone KOHAq, al sol dilute caustic potash and ammonia Ppd by NaHCO, from solutions of its salts Inactive to light (Hesse, A 176, 198) Can be extracted both from acid and alkaline solutions by shaking with benzene or chloroform (Plugge, Ph. [8] 20, Narceine is a sommiferous poison, 5 g

being probably a fatal dose

Reactions -1 Zinc and HOlAq form a small quantity of an amorphous base C.H., NO. or C.H., NO. (Beckett a Wright, C J 28, 701) — 2 Water at 150° carbonises it —8 Chromic acid mixture yields hemipic acid (10 p c.) and methylamine (Beckett a Wright, C J 29, 467)—4

Ferric chloride forms hemipic, but no opianic acid. Hemipic acid is also formed, though in smaller quantity, by oxidation by KMnO, or by

MnO, and H,SO, Alkaline KMnO, forms narceïc acid (v infra) —5 Conc HNO, yields oxalie acid —6 Boiling caustro potash gives off ammonia and NMe, and forms a sparingly soluble acid C₂₂H₂₂NO₅ [210°] —7 Potash-fusion yields protocatechuic acid

Tests -1 Weak wodine solution colours solid narceine dark blue, the colour not being removed by ammonia The blue colour is destroyed by boiling water -2 Conc H₂SO₄ turns it brown, and then dissolves it, forming a yellow solution Narceine is not coloured by diluted sulphuric acid, but on heating over a water bath a violet red colour appears, which ultimately becomes cherry red If the red liquid be cooled and a trace of HNO, or KNO, be added, bluish-violet stripes appear (Plugge, Ar Ph [3] 25, 425) -3 Erdmann's solution gives a brown colour, turning reddish-brown on heating -4 Chloride of wodine forms a greenish yellow pp, which dissolves on heating (Dittmar, B 18, 1612) 5 Potassium chromate gives no pp in cold saturated solutions of salts of narceine, but in hot solutions there is formed a pp of narceine chromate and free narceine (Plugge, Ar Ph [3] 25, 793) -6 Narceine is a feeble base, so that its salts may be titrated by standard alkali as if they contained no base (Plugge, Ar Ph [3] 25, 45) -7 When strongly heated it gives off vapours smelling like herring brine (Hesse) -8 Chlorine-water followed by ammonia gives a red colour

Salts -B'HCl (dried at 100°) concentric needles, sol water and alcohol S 36 —
B'HCl 2½aq (Pettt, Bl [2] 18, 534) S 7—
B'HCl 3aq (Wright, C J 27, 109)—B',HCl (Pett)—B',HCl (P)—B',HPtCl, (dried at 100°) crystalline powder [195°] Golden 100°) crystalline powder [195°] Golden needles (Claus) —B'₂H_PtCl₂2aq amorphous pp changing to prisms (Hesse, A 129, 250) —B',H_SO₄,10aq crystals (Beckett a Wright, C J 27, 69) —B'₂H₂SO₄ —B'₄H₂SO₄ —B'₄H₂SO₄ -Mercurico-chloride, oily at first, ultimately crystallising in concentric prisms (Hesse) [118°-122°] (Roser, A 247, 175) — B'₂H₁I₂ slender needles (Jörgensen, B 2, 400) — B'HI₂: needles (from alcohol)

Methylo-rodide B'Mel [173° uncor]; colourless needles (Claus a Kitzefeld, B 18, 1569)

Methylo-chlorede B'MeOl [210° uncor], soluble small white needles easily (B'MeCl), PtCl, nearly insoluble yellow powder Methylo-netrate B'MeNO, [186° uncor]; small white soluble needles (C a. R.)

Ethylo-sodede B'Etl granular crystals (Beckett a Wright, C J 28, 708) Yields alkaline B'EtOH which is B'Etl 2aq readily split up into narceine and alcohol

Ethylo-bromide B'EtBr [165° uncor], fine white soluble needles — (B'EtBr)CdBr: small colourless needles (C a R)

Ethylo-chlorede B'EtCl. [170° uncor], tening yellow crystals [170° uncor], small colourless needles — (B'EtCl),PtCl, glistening yellow crystals [170° uncor] (C a R) — (B'EtCl)HgCl, aq [127°], white crystalline pp.

Ethylo-netrate B'EtNO; : [155° uncor], long colourless silky needles, sol. water (C a R).

Ethylo-oxalate B'Et,C.O. [0

uncor], glistening needles (containing 6aq)

Bensylo-chlorede B'O,H,Cl. [162° uncor.], fine white needles, v. sol. hot water and alcohol, insol ether -(B'C,H,Cl),PtCl4. [165°] uncor]; yellow crystalline powder

Methyl narceine C₂₂H₂₂(CH₃)O₂N [175° uncor] Formed by adding KOH (2 pts) to a boiling solution of narceine methylo-iodide (1 pt) in 10 pts of water (Claus a Ritzefeld, B 18, 1770) 1573) Fine colourless needles V sol alcohol. sl. sol water, nearly insol ether

Bensyl-narceine $C_{23}H_{28}(C_7H_7)O_9N$ uncor] Formed by the action of aqueous KOH upon narceine benzylo-chloride (Claus a Ritzefeld, B 18, 1574) Long white needles V, sol Alkalıne alcohol, nearly insol water and ether reaction —(B'HCl)2PtCl4 2aq [128° uncor 1.

dark yellow crystalline pp
Narceic acid ClisHisNO [184°] Formed
by oxidising narceine with KMnO (Claus a Formed Meixner, J pr [2] 37, 3) Prisms (containing 3aq), v sol alcohol, ether, chloroform, and hot water Decomposes at 180°-200° into CO₂, dimethylamine, and di-oxy-naphthalene dicarboxylic acid C₁₂H₈O₆ Not acted upon by FeCl₃ —Na₂A''' —Na₂HA''' 5aq [85°] —NaH₂A''' 4½aq —

Ba,A", 5aq —Ag,A"'

\[\psi. \text{Narcotine} \]

\[\psi \text{Narcotine} \]

\[\psi \text{Narcotine} \]

\[\psi \text{ARCOTINE} \]

\[\cdot \text{2.2H}_{25} \text{NO}, *.6 \]

CH CNMe CH, CH, C CH C(OMe) CO CH, O CO C C(OMe) C(OMe) -Ò CÌI-

(Roser, A 254, 357) Mol w 413 [155°] (Wynter Blyth, C J 33, 317), [176°] (Hesse) S 014 at 100° S (85 pc alcohol) 1 in the cold, 5 at 78° (Duflos, B J 12, 214) S (ether) 77 in the cold, 21 on boiling (Duflos), 6 at 16° (Hesse) S (isoamyl alcohol) 325 in the cold S (benzene) 461 in the cold (Kubly, J 1866, S (chloroform) 38 (Pettenkofer) (EtOAc) 17 (Henry) $[a] = -130^\circ$ in ethereal solution (Bouchardat, A Ch [3] 9,213), -185° m alcoholic solution, -207° in chloroform at 22 5° (Hesse, A 176, 192) Contained in opium to the amount of 5 to 8 pc, and was the first alkaloid extracted therefrom (Derosne, A Ch 45, 257, Robiquet, A Ch. [2] 5, 275, Dumas a Pelletier, A Ch. [2] 24, 188, 50, 269, Liebig, A 6, 35, Brandes, A 2, 274, Couerbe, A Ch [2] 59, 169, A. 17, 174, Regnault, A Ch [2] 68, 137, Wöhler, A 50, 1, Blyth, A 50, 29, Werthem, A 70, 71, 73, 208, Fluckiger, J 1869,

Preparation -1 The mother-liquor obtained in the preparation of morphine $(q \ v)$ by Gregory's process is ppd by ammonia, and the pp recrystallised from boiling spirit (Anderson, A 86, 179) —2 Opium is extracted with dilute HCl and the bases ppd by KOH The bases are treated with oxalic acid to ppt papaverine, and the filtrate from acid papaverine oxalate ppd by ammonia The pp is recrystallised from alco hol (Hesse, A Suppl 8, 284) -3 Cone aqueous NaOAc added to a solution of the hydrochlorides of the opium bases throws down narcotine and papaverine The pp is redissolved in dilute HÖlAq and mixed with K_{*}FeCy_e which ppts papaverine ferricyanide From the filtrate the narcotine is ppd by ammonia (Plugge, Ar Ph [8] 25, 343)

Properties -Trimetric prisms, or groups of

needles Cannot be sublimed If cooled slowly after melting it forms slender radiating needles.

Insol cold water, m sol alcohol and ether. Lævogyrate in neutral solutions, dextrogyrate in acid solutions Insoluble in aqueous potash, nearly insol NH₂Aq Dissolves in boiling baryta-water, but ppd therefrom by NH₂Aq Its solutions do not give a blue colour with FeCl, Narcotic poison, 8 g killing a cat Not acted upon by Ac,O

Reactions -1 Distillation with cone HIAq yields MeI (3 mols) (Matthiessen a Foster, Tr 1863, 345, C J 16, 342, A Suppl 6, 60) -2 Conc HolAq at 110° yields MeCl and, succes sively, di-methyl-nornarcotine, methyl nornarcotine, and normarcotine (Matthiessen a Foster, C J 21, 257, Matthiessen, Pr 17, 337, Matthiessen a Wright, Pr 17, 340) Distillation with equal volumes of H₂SO₄ and water gives MeHSO, and the three bodies last mentioned (Armstrong, C J 24, 56) -3 Boiling dilute KOHAq has no action, but potash-fusion at 200°-220° yields trimethylamine and other volatile amines (Hofmann, A 75, 367) -4 Dilute mtric acid at 50° forms meconin, opianic acid, hemipic acid and cotarnine —5 Distillation with HCl and platinic chloride also yields opianic acid and cotarnine The same products are formed by oxidation with H₂SO₄ and MnO₄ (Wöhler) -6 Water at 140° splits it up into meconin and hydrocotarnine (Beckett a Wright, C J 28, 583) Sodium-amalgam gives the same products -7 Iodine acting on an alcoholic solution of narcotine forms tarconine methylo periodide and iodo tarconine methylo periodide

(Jörgensen, J pr [2] 2,446, Roser, A 245,317)

Tests—1 Cono H,SO, forms a yellow liquid which, when heated becomes orange red and finally violet red (Husemann, A 128, 305) -2 H₂SO₄ containing a little HNO₃ gives a reddishyellow colour —3 Does not liberate iodine from iodic acid -4 Does not reduce alkaline K, FeCy. (Kieffer, A 103, 277) -5 Bromine gradually added to a boiling solution of narcotine in dilute HClAq forms a rose coloured liquid, the colour being destroyed by excess of bromine -6. Potassio mercuric iodide forms a yellowish white pp (Groves, C J 11, 97) Phosphomolybdic acid, pierie acid, potassium sulphocyanide, and auric chloride also give pps in solutions of salts of narcotine -7 A solution of potassium chrom ate added to one of a salt of narcotine, ppts free narcotine (Plugge, Ar Ph [3] 25, K2Cr2O, ppts narcotine bichromate -8 Salts of narcotine require, on titration, the same amount of alkalı for neutralisation as if the base were absent (Plugge, Ar Ph [8] 25, 45) -9 Chloride of rodine gives a curdy yellowish pp (Dittmar, **B** 18, 1612)

Salts -B'HCl Needles, v sol water $[a]_D = -47^\circ$ to -50° in a 2 p c solution contain ing excess of HCl $[a]_p = -1045^\circ$ in a 2 p c solution in 80 pc alcohol containing excess (1 mol) of HCl (Hesse, A 176, 192) — B'HCl aq (Dott, J 1884, 1389) — B', HCl (Beckett a Wright, O J 29, 164) -B', HCl -B', HCl (B a. W) — Mercurico chloride white pp (Hin terberger, A 82, 311) — B'₂H₂PtCl₂ yellow crystalline pp (Blyth) Decomposed by boiling water (De Connick, Bl [2] 45, 181) — B'₂H₂PtCl₂ 2aq (Hesse) — B'₂H₃SO₄4aq (Dott) — B'₂H₂Cr₂O₇ — B'HI, shining lamine, converted by boiling alcohol into tarconine periodide CisHiiNOsHIs

Jörgonsen, B 2, 460) —B', HOAc aq needles (Dott) — Binoxalate v e sol water -Cyanurate B'H₃O₂C₂N₃ 1₃aq, needles [c 175°], v sl sol water (Claus, J pr [2] 38, 229) Methylo-chlorads B'MeCl Formed by

heating narcotine with MeI and decomposing the viscid B'MeI with AgCl (Roser, A 247, 168) Groups of needles, v sol water and alcohol Yields ψ narceine (v infra) on distillation with aqueous NaOH $-B'_2Me_2PtCl_s$

Ethylo rodrde B'Etl (How, A 92, 327)

Ethylo chloride *B'EtCl Yields ψ me thyl narceine [173°] on treatment with NaOHAq

-B′,Et₂PtCl Nornarcotine C, H, NO, Obtained by heat

ing narcotine with fuming HIAq (Matthiessen a. insol alcohol and ether ton of its hydral Wright, Pr 17, 340) White amorphous mass, also by water The hydrochloride is tasteless, and its solution gives with KOH, Na2CO2, and NH₃ pps soluble in excess, and with platinic

chloride a yellow pp, quickly turning brown

Methyl derivative C2H10NO, Formed by heating narcotine with HClAq for some days White amorphous mass, almost insol water, insol alcohol and ether Its solution in cond HClAq is ppd by water Astringent taste The platinochloride is a yellow pp, slowly turning brown The ppd base is soluble in excess of NH3Aq and Na2CO3Aq but sl sol KOHAq

Di-methyl derivative C21 H21 NO, Formed by heating narcotine with HClAq for 2 hours or with diluted H₂SO₄ at 100° White amorphous mass, almost insol water, v sol alcohol, sl sol ether Its solution in HClAq is ppd by water Its hydrochloride tastes bitter The platinochloride is a yellow pp The ppd base is insol Na₂CO₂Aq, sl sol NH₂Aq, sol KOHAq

ψ-Narceine C₂₃H₂₇NO₈ [c 175°] Formed by boiling narcotine with MeI, decomposing the resulting methylo iodide by AgCl, adding an equivalent amount of NaOH, and distilling with steam (Roser, A 247, 169) Slender white needles (containing 3aq), v sol alcohol and hot water, sl sol cold water, insol ether Dissolves in aqueous KOH and NH₃, but is reppd by CO₂ Inactive to light Coloured blue by iodine Cone H.SO, forms a brownish yellow solution, turned dirty violet on heating Chlorine water followed by ammonia gives a red colour cording to Roser, this body is probably identical with narceine —B',H,SO, 2aq tufts of needles —B'HCl3aq —B',H,FtCl, [198°] Thin needles, insol water —Aurochloride [130°], yel-[130°], yellowish red needles -- Mercury double salt [1230

ψ-Methyl-narceine C₂₄H₂₉NO₃ ψ-Homo-narceine [173°] Formed by passing steam through a mixture of narcotine ethylo chloride and aqueous NaOH (Roser, A 247, 173) needles (containing 3aq), v sol water and alcohol, insol ether Gives a blue colour with iodine The hydrochloride and sulphate are v sol water -B'2H2PtCl 2aq small yellow needles

Teropiammon C.H. NO12. A crystalline sompound, insol. water, found among the pro-

ducts of the action of dilute HNO, on narcotine (Anderson) It forms a crimson solution in H₂SO₄ and yields NH₃ and opianic acid on boiling with potash.

Cotarnine C12H15NO4 \$.0

 $\begin{bmatrix} 2 & 1 & 4 & 5 \end{bmatrix}$ OH, $\begin{bmatrix} 0 \\ 0 \end{bmatrix}$ C, H(OMe)(CHO) OH, OH, NHMe

(Roser, A 254, 354)

oser, A 254, 354) [133°]
Formation —1 By the oxidation of narco-Formation —1 By the exidation of narcotine by MnO₂ and H_2 SO₄ (Wöhler, A 50, 19, Matthiessen a Foster, Pr 11, 55, Beckett a Wright, C J 28, 575), by platinic chloride (Blyth, Mem C J 2, 168), by dilute intric acid (Anderson, C J 5, 266, A 86, 196) or by K_2 Cr₂O₇ (M a F)—2 By the exidation of hydrocotarnine (Beckett a Wright, C J 28, FOO1

Properties —Colourless needles, sl sol water, v sol alcohol and ether Decomposed on fu-A solution of its hydrochloride is neither ppd by HCl nor by water Its salts taste bitter The freshly ppd base dissolves in excess of aqueous NH₃ and Na₂CO₃, but is v sl. sol. KOHAq Decomposes on fusion Cotarnine is not poisonous

Reactions -1 Nitric acid forms a red solution and, on heating, oxidises it to apophyllenic and oxalic acids -2 Aqueous HCl, HI, or H2SO4 at 140° yields MeCl, MeI, or MeHSO4 and cotarnamic acid -3 Zinc and dilute HClAq yield hydrocotarnine—4 Bromine-water forms $C_{12}H_{12}Br_2NO_3$ (Wright, C J 32, 533) Bromine water added to a solution of cotarnine hydro chloride forms C₁,H₁₂Br₃NO₃HBr, a crystalline pp [190°-200°] (Von Gerichten, B 14, 311)

Salts -B'HCl 2 aq long silky crystals (Blyth) -B'2H2PtCl6 lemon-yellow crystalline pp, or dark red six sided prisms -B'HClHgCl. pale-yellow pp -B'HBr 2aq -B'HI vellow needles, si sol cold water and alcohol (Roser, A 249, 156) —B'HI, [142°] (Jorgensen, J pr [2] 2, 455)

Bensoyl derivative C12H14BzNO42aq [123°] Formed by shaking cotarnine with BzCl and dilute NaOHAq (Roser, A 254, 335) Long needles, insol water, v e sol hot alcohol

 $Ox_{2}m$ $C_{12}H_{5}NO_{2}(NOH)$ [168°] insol water, m sol alcohol, sol alkalis -B'HCl small yellow needles, v sol water, m sol alcohol -B',H,PtCl, yellow crystalline pp decomposed by boiling water

Oxim of the benzoyl derivative C₄H₄O₅(CH NOH) C₂H₄ NMeBz [166°] Formed by warming benzoyl cotarnine with alcoholic hydroxylamine hydrochloride Small pointed crystals, insol water and ether, v sol alcohol, sol NaOHAq

Methyl-cotarnine

Methylo-rodide C11H11O4NMe,I Formed by warming cotarnine with MeI (Roser) Yellow needles, sl sol cold water and alcohol composed by boiling NaOHAq into cotarnone and NMe,

Methylo chlorade C,H,O,NMe,Cl 3aq. Formed from the iodide and AgCl Crystals (from water) On warming with alcoholic hydroxylamine hydrochloride at 100° it yields C₁₄H₁₆ClN₂O₂ 2aq or C₆H₂O₃(CN) C₂H₄NMe₃Cl a crystalline body, v sol water, converted by hot NaOHAq into NMe, and C,H,O,(ON).CH CH, [16 The last body forms a dibromide [140°]. (C, H,1O,NMe,Cl),PtČl,

C₁₉H₁₄BrNO₄ [100°] Bromo-cotarnine Formed by treating hydrocotarnine hydrobromide with bromine-water (Wright, O J 32, 525) Crystals (from ether), decomposing at 100° Reduced by zinc and HClAq to brome-hydrocotarnine [78°] — B'HBr — Crystals, v sol water Above 200° it melts, gives off gases, and forms a small quantity of tarconine hydro-bromide, together with a blue substance Cath, N.O. HBr insoluble in alcohol

Cotarnone C11H10O4 & 6 CHO C.H.O, CH CH. [78°] Formed by warming methyl cotarnine methylo chloride with aqueous NaOH (Roser, A 249, 163) Plates (from alcohol), slightly volatile with steam Inscold water, m sol alcohol, ether, and HOAc

Oxim C₅H₆O₃(CH NOH) CH CH₂ [132

[132°] Slender needles (from dilute alcohol).

Cotarn-lactone $C_{11}H_{10}O_{e}$ is c $CH_{2} < \begin{matrix} O \\ O \end{matrix} > C_{e}H(OMe) < \begin{matrix} CO & O \\ OH(CH_{2}OH) \end{matrix} >$ [154°] Formed by oxidising cotarnone with KMnO. (Roser, A 254, 341) Prisms, sl sol cold alcohol or water Forms with baryta the salt Ba(C11H11O2)25aq

Acetyl derivative C₁₁H₆AcO₆ [174°] Bensoyl derivative C₁₁H₆BzO₆ [184°] Cotarnic acid C10HaO, 1.6

 $CH_2 \stackrel{O}{\bigcirc} C_e H(OM_e)(CO_2H)_2 \begin{bmatrix} 1 \\ 2 & 5 & 6 \end{bmatrix}$ [178°] Formed by oxidising cotarnone or cotarn lac

tone with aqueous KMnO₄ (Roser, A 249, 165, 254, 345) Plates Forms, on melting, the an hydride C₁₆H₄O₆ [162°] On heating with P and HIAq it yields gallic acid HClAq at 100°

forms OH₂ O O H₂ (OMe) CO₂H [210°]

Bromine in HOAc produces the compound $OH_2 < O > C_e Br_s (OMe)$ [160°]

Salts — KHA"21aq needles, v sol. water -BaA": plates -AgaA

Hydrocotarnine O12H15NO3 16 $OH_2 < O > C_2H(OM_e) < OH_2OH_2OH_2$ [50°] (H),

[55°] (B a W) Occurs in opium (Hesse, A Suppl 8, 326) Formed by reducing cotarnine with zine and HClAq, and, together with meconin, by the action of zinc and HClAq on narcotine (Beckett a Wright, C J 28, 577) is also formed in small quantity (2 to 5 p c) in the preparation of opianic acid by the oxidation of narcotine. Monoclinic prisms (from ether), v sol alcohol and benzene The crystals contain water of crystallisation (aq) Cone H.SO. forms a yellow solution, changing on heating to crimson and, finally, to a dirty violet colour Easily oxidised to cotarnine Not attacked by Ac O Bromine added to a solution of its hydrobromide forms C₁₂H₁₄BrNO, [78° cor], which yields the crystalline salts C12H14BrNO3HBr and

(C₁₁H₁,BrNO₂)₂H₂PtOl₂ Salts—B'HCl aq —B'₂H₂PtOl₃—B'HI. S 2 at 18°—B'HBr 13 aq

Ethylo-sodeds B'Etl White micaceous plates, sl. sol water Yields (B'EtCl [100°], both crystalline, and (B'EtCl), PtCl. Yields (B'Et) CO, 4aq,

Acetyl-hydrocotarnine-acetic acid CicHieNO. [201°] Formed by boiling cotarnine (1 pt) with acetic anhydride (10 pts) for 14 hours Small needles Sol alcohol and benzene, sl sol boil ing water, insol cold water, and ether -A'Ag white pp —A',Ca very soluble small needles

Ethyl ether A'Et [113°], white feathery
needles (Bowman, B 20, 2431).

Oxy-hydrocotarnine methylo-iodide $\mathrm{OH_2} \overset{\mathrm{O}}{\underset{>}{\bigcirc}} \mathrm{O_0H}(\mathrm{OMe}) \overset{\mathrm{OH}(\mathrm{OH})}{\underset{>}{\bigcirc}} \overset{\mathrm{NMe_1}}{\underset{>}{\square}}$

Methyl derivative C₂H₂O₂ C₂H₂(OMe)NMe₂I [178°] Formed by the action of MeI in the cold on a solution of cotarnine in MeOH (Roser, A 254, 360) needles, v sol hot water and alcohol Ppd unchanged by adding NaOH to its warm aqueous solution Boiling with water and Ag₂O expels

NHMe₂.—(O₁,H₂,NO₄Cl)₂PtCl₄ orange pp Ethyl derivative C₁,H₁,O₅(OEt)NMe₂I [168°] Formed by the action of MeI on a cold solution of cotarnine in EtOH Plates, v e sol

water and alcohol.

Isobutyl derivative O1.H1,ON(OEt)I

Formed by heating cotarnine with aqueous HCl at 140° (Matthiessen a Foster, A Suppl 2, 379, Gerichten, B 14, 310) Yields apophyllenic acid on oxidation by dilute HNO₃ —C₁₁H₁₁NO₃HCl aq White needles, sl sol cold water On treatment with nitrous acid or on exposure to air its solu tion becomes green, with red fluorescence, and exhibits a spectrum resembling that of chloro phyll

Tarconine C11H2NO2 Formed by heating bromo cotarnine hydrobromide at 200° (Wright, C J 32, 535) or tarconine methylo chloride with cone HClAq for 4 hours at 150° (Roser, 4 245, 821) Ppd from solutions of its salts by KOH, but not by Na₂CO₃ Its hydrochloride heated at 200° forms a blue base C20 H14N2O4 forming the blue salts B'₄H₃Br₃ and B'₂H₂SO₄—
Salts B'HCll₂aq needles, v e sol water
and alcohol —B'₂H₂PtCl₃ insol alcohol

Methylo-vodide B'MeI Formed by the

action of H2S on the periodide which is formed by boiling narcotine in alcoholic solution with odine and some HO! Tutts of yellow needles (from water or alcohol) —B'MeI, [160°] Red dish brown needles (from alcohol or HOAc) — B'MeI, (Jörgensen) -B'MeBıI,

B'MeCl Methylo-chloride needles — (B'MeCl), PtCl, yellow crystalline pp, sl sol water — B'HAuCl,

Bromo-tarconine C11HsBrNO. 16

O₄H₂BrO O₂H₂N<00 [285°-288°] Formed by heating the hydrobromide of the compound $C_{12}H_{12}Br_2NO_2$ (v Cotarrine, Reaction 4) with water at 180° (Wright, Gerichten, A 210, 84) Orange red needles (containing 2aq), becoming crimson and anhydrous at 100° Sl sol cold water, msol. ether Water at 160° splits it up into cupronine and tarnine Cone HClAq at 120° forms nartic soid, tarnine, CO, and CO Chromic acid mixture yields bromoform and apophyllenic acid Bromine-water added to a solution of its hydrochloride yields cuprine, bromo apophyllenic acid, and dibromo apophylNARINGIN 497

lin. Distillation over soda-lime yields pyridine. -B'HCl 2aq crystals, sl sol cold water.-B'HBr 2aq -B'₂H₂PtCl₄ needles (from hot conc. HClAq)

Methylo-chlorede CuH.BrNO.MeCl slender needles, v e sol water, m sol alcohol -

(B'MeCl)₂PtCl₄ —B'MeAuCl₄

Methylo-bromide C., H.BrNO.MeBr Formed by the action of bromine water on an aqueous solution of tarconine methylo chloride. the perbromide first formed being decomposed by H₂S (Roser, A 245, 324) Long needles (containing aq), changing on standing to flat prisms
—B'MeBr. [165°] Yellow rectangular plates (from alcohol or HOAc)

Methylo-rodide C, H, BrNO, MeI [204°] Formed from bromo tarconine and MeI (Gerichten, A 210, 170) Yellow needles, sol water, insol ether Turns brown at 170° Boiling baryta water converts it into formic aldehyde and methyl bromo tarconic acid Moist Ag.O forms the hydroxide crystallising in small red

needles

Ethylo-rodide C, HBRNO, EtI [206°] Formed from ethyl iodide and bromo tarconine

Yellow needles Yields (B'EtCl)2PtCl

Iodo-tarconine C₁₁H₈INO₃ Formed by heating its methylo chloride at 180° (Roser, A 245, 319) Crystallises from water in yellowish red needles (containing aq), becoming dark red on drying -B'HCl 2aq silky yellow needles, v sol water, sl sol HClAq

Methylo-chloride C,,H,INO,MeCl aq Formed from the methylo-rodide and AgCl Yellowish white needles (from alcohol), m sol water —(B'MeCl)₂PtCl₄ sol hot needles, sl water - B'MeAuCl, needles (from hot water)

Methylo rodide CuH, INO, MeI Formed by the action of iodine on narcotine in alcoholic solution, the resulting periodides being decomposed by H₂S (Roser, A 245, 317) Yellow needles, changing on standing to prisms, almost insol cold water, al sol hot alcohol— [171°] Needles, sl sol alcohol

Methyl tarconic acid CnHijNO, [244°] Lormed from the aqueous solution obtained by the action of Ag₂O and water on tarconine methylo chloride by boiling alone or with baryta (Roser, A 245, 322, 254, 366) Not a true homologue of tarconic acid Thin yellow needles (containing 2aq), v sol hot water, alcohol, mineral acids, and KOHAq, insol. ammonia—C₁₁H₁₁NO₃HClaq white prisms or needles, turns yellow on drying at 100°.— C₁₁H₁₁NO₄H₂SO₄ Saq white prism (C₁₁H₁₁NO₄)₂H₂SO₄ 6aq yellowish crystals prisms

Bromo - methyltarconic acid C11H10BrNO. Formed by boiling bromo tarconine methylo hydroxide with baryta water (Gerichten, A 210, 79, Roser, A 245, 826) The result is decomposed by H₂SO₄ or HOAc The ppd Ba Yellow prisms (containing 2aq), insol cold water and ether, sl sol hot alcohol Darkens at 215° Heated with cone HClAq it yields MeCl, HBr, and tarconic acid —CuA'₂ —BaA'₂ yellow pp-(HA'HCl)₂PtCl₄ needles, m sol dilute HCl

Ethyl - bromo - tarconic acid CigH12BrNO [225°] Formed by the action of baryta on bromotarconine ethylo iodide (or ethylo hydroxide) (Gerichten, A 212, 182) Yellow needles (containing 2 aq), v sl sol cold water, v sol. alco-Vol. III

hol, insol ether Its aqueous solution is neutral. Cone H₂SO₄ forms a yellow solution Cone HClAq converts it, on heating, into EtCl, HBr, and tarconic acid—HA'HCl yellow needles—

(HA'HCl), PtCl, —Cu'A,

Tarconic acid C₁₀H, NO, Formed by heating bromo methyl tarconic acid with conc HClAq at 155° (Gerichten, A 212, 184) Slender yellow needles, turning brown in air Its alkaline solu tion is brown, becoming greenish blue on standing It reduces AgNO, in the cold —HA'HCl prisms, m sol hot water, insol cold alcohol FeCl, colours its solution red

Nartic acid C20H16N2O6 Nartine Formed by heating bromo tarconine or tarnine with conc HClAq at 130° (Gerichten, A 212, 194, 212, 170) Yellow needles, decomposing at 200° without melting Turns brown in air NaOH does not ppt it from acid solutions Its solution in NaOHAq turns greenish blue when exposed to air Reduces AgNO, KMnO, oxidises it to a pyridine carboxylic acid On distillation with soda lime it yields pyridine.—H,A"H,Cl,. [above 275°] Yellow needles, m sol water —H,A"HCl yellow needles, sl sol water

Tarnine C₁₁H₀NO₄ [above 290°] Formed by heating bromo-tarconine with water at 130° (Gerichten) Orange needles (containing 1 aq) m sol hot water and dilute alcohol, insol ether-*B'HCl yellow needles, sol water,-B₂H PtCl₆ Decomposed by boiling water

Cupronine C₂₀H₁₈N₂O₆ Formed, together with tarnine, by heating bromo tarconine with water at 140° (Gerichten, B 14, 315, A 210, 190°) Black powder, insol hot water, alcohol, and ether Forms a brown solution in aqueous NaOH or Na,CO, Cone H,SO, forms a magentared solution, changing to violet on dilution Conc HClAq does the same -B'HCl copperv needles—B'HBr bluish green needles with coppery lustre, sl sol water, forming a blue solution

Cuprine C,1H,NO, Formed by the action of bromine on a solution of bromo tarconine hydrobromide (Gerichten, A 210, 89) Minute blue needles with coppery lustre, sol water and alcohol, insol ether Weak base, the hydrochloride crystallising in concentric groups of needles, the platinochloride being a deepblue flocculent pp

Apophyllenic acid is the mono methyl ether of Pyridine dicarboxylic acid

Di bromo-apophy.lin v vol i p 553

Oxy-narcotine $C_{2}H_{2}NO_{8}$ Crystals which remain undissolved in the process of purifying narceine (Beckett a Wright, C J 29, 461) Small crystals (from alcohol), v sl sol water and alcohol, msol ether, nearly msol benzene and chloroform Ppd from solutions of its salts by NaOH and Na₂CO₃, but redissolved in excess Oxidised by FeCl, to hemipioscid and cotarnine -

B'HCl 2sq orystals —B',H_PtOl,

NARINGIN C₂₁H₂₂O₁₁ Aurantum Hesper
idme [171°] S 33 in the cold [a]₀ = -84 5 -87 6 in alcoholic solution in aqueous solution, (W), $[a]_1 = -64.6$ (H) Occurs in the flowers The dry and other parts of Citrus decumana orange-blossoms contain about 2 p c It crystallises on cooling from the liquor left in the still after distilling over the oils with steam (Hoffmann, Ar Ph [3] 14, 139, Will, B 18, 1311,

KK

20, 295) White crystals (containing 4aq), nearly insol cold water, sol alcohol, insol ether Has a very bitter taste Split up by dilute H2SO (3 p c) at 95° quantitatively into naringenin and isoduleite. It dissolves in alkalis with a yellowishred colouration Ferric salts produce a brownishred colouration with dilute aqueous solutions By sodium-amalgam it is converted into a colouring matter which dissolves in alcohol with a red colour and bluish fluorescence

Naringenin C₁H₁O₅ probably
[4 1] C₅H₄(OH) CH CH CO O C₅H₅(OH)₂ [1 8 5]
[248°] Formed, together with isodulotte, by heating naringin with dilute (2-3 p c) H₂SO₄ on the water bath Glistening colourless, tasteless, and odourless crystals V sol alcohol, ether, and benzene Dissolves in alkaline hydrates forming yellow solutions, and is reprecipitated by Ferric salts give a brown-red colouration By sodium-amalgam it is converted into a colouring matter which dissolves in alcohol with a red colour and bluish fluorescence By boiling with concentrated aqueous NaOH it is decomposed into phloroglucin and p coumaric acid (Will, B 18, 1322, 20, 297)

Maringenic soid is p Coumaric acid NARTIC ACID v NARCOTINE.

NATALOIN v ALOIN

The name given by Auer NEODYMIUM von Welsbach to that constituent of didymium which yields rose coloured salts (v DIDYMIUM, vol 11 p 383, cf METALS, RARE, this vol p 240)

NEOSSIDINE v PROTEIDS, Appendix C.

NEOSSINE v PROTEIDS, Appendix C

NERIODOREIN A bitter yellow powder, extracted by alcohol from the bark and wood of Nersum odorum, an Indian plant prescribed for leprosy (Greenish, Ph [3] 11, 873) It is sol water, insol chloroform. Its solution is ppd by tannin and by ammoniacal lead acetate, and reduces Febling's solution

Neriodorin A bitter resin, accompanying the preceding body, sl sol water and alcohol, v

sol CHCl,

NEURIDINE C,H,N, A product of the putrefaction of flesh, appearing on the second day and disappearing about the fourth day (Brieger, B. 1b, 1187, 1405, Booklisch, B 18, 86; Gautier, Bl [2] 48, 12) It also occurs in fresh human brain (Brieger, J Th 1884, 92) Gelatinous mass with disgusting smell, v e sol water, insol alcohol and ether Very poisonous (G) Its solution is ppd by HgCl, and by lead Yields di- and tri- methylamine on acetate boiling with NaOHAq -B"H2Cl, needles, v. sol water, insol alcohol and ether -B"H2PtCl.

NEURINE C.H., NO. + 6 CH₂(OH) CH₂.NMe.OH **Cholins** Dr-methyloxy-ethyl-amine methylo-hydroxide Tri-methyloxethyl ammonium hydroxide Sincaline

Occurrence -In cotton seeds (Böhm, J pr. [2] 30, 37), in putrefying flesh (Gautier, Bl [2] 48, 18), in germinating pumpkin sprouts (E. Schulze, H. 11, 365), in the seeds of Trigonella Fanum gracum (Jahns, B. 18, 2518), in the seeds of vetch, Vaca satura (Schulze, B. 22, 1988). 1827), in hops and beer (Griess a. Harrow, C J 47, 298, B. 18, 717), in areca nuts (Jahns, B 23, 2972), in the fly again (Harnack, J 1876, 803), in herring brine (Bocklisch, B 18, 1928),

in ergot of rye (Brieger, H 11, 184); and in

best root juice (Lippmann, B 20, 3201)

Formation—1 By boiling the bile of pigs or oxen with baryta (Strecker, C R 52, 1270, A. 123, 853, Dybkowsky, J pr. 100, 163, Huiner, J pr [2] 19, 302) —2 By boiling ox-brain with baryta (Liebreich, A 184, 29, Baeyer, A 140, 306) -3 By extracting yolk of egg with ether and alcohol, evaporating the extract, and boiling the residue with baryta (Diaconoff, J1867, 776, 1868, 780) In this preparation two similar bases occur, containing 34 and 32 p c Pt in their platinochlorides (Hundeshagen, J pr. [2] 28, 247) —4 Together with glycero-phosphoric acid, oleic, and palmitic acids by the action of alkalis on lecithin (Liebreich, Gobley, C R 70, 1297, Bokay, H 1, 157, 12, 148) 5 Together with sinapic acid and barium sulpho cyanide, by heating sinapine sulphocyanide with baryta water (Claus a Keesé, Z [2] 4, 46)

Syntheses -1 By heating trimethylamine (5 g) with glycolic chlorhydrin (10 g) at 100°, the resulting chloride HO CH2 CH2 NMe, Cl being decomposed by moist Ag,O (Wurtz, C R 65, 1015, 68, 1434, A Suppl 6, 116)—2 By the union of ethylene oxide with trimethylamine

(Wurtz, A Suppl 6, 201)

Properties -Strongly alkaline syrup, decom posed on boiling in concentrated aqueous solu tion into glycol and trimethylamine HIAq and P at 140° forms C,H,I NMe,I Weaker HIAq yields C,H,I NMe,Cl Yields muscarine and betaine on oxidation Not poisonous

Salts — C₂H₄(OH)NMe₃Cl Dimorphous usually as long needles, sometimes in thin tri metric plates -(C₂H₄(OH)NMe₂Cl)₂PtCl₄ morphous orange prisms (from warm saturated solution), reddish brown trimetric tablets from a cold saturated solution, or regular octahedra from a solution containing 15 pc of alcohol The first and third forms left in contact with their mother liquid change into the second form (Hundeshagen, J pr [2] 28, 245)—(O₂H₄(OH)NMe₂Cl)AuCl, yellow needles, sl sol cold water—C₂H₄(OH)NMe₄I Formed from Formed from $C_2H_4(OH)NMe_2$ and MeI (Knorr, B 22, 1116)

Acetyl derivative of the chloride C₂H₄(OAc) NMe₃Cl - C₇H₁₆NO₂ClAuCl₃ nodules

NEURO-KERATIN v PROTEIDS, Appendix C NICKEL At w. 586 Mol w unknown, as element has not been gasified [c 1400°-1420°] (Schertel, N 22, 543), [c 1450°] (Pictet, C R 88, 1317) SG 897 to 926 (Rammels berg, J 2, 282, for other values v Clarke's Table of Specific Gravities [new ed], 12) SH 14° to 97° 10916 (Regnault, A Ch [3] 63, 1) $V_t = V_o (1 + 3 \times 00001279t) t = 40^\circ (Fizeau, C \hat{R})$ 68, 1125) E C at 0° (Hg at 0°=1) 7 374 (Matthessen a Vogt, P M [4] 26, 242) S V S c 6 5 H.C [Ni², 0², 3H²O] = 120,380 (Th 3, 307) For spectrum of N1 (ultra violet) v Liveing a. Dewar, Pr 43, 430

Occurrence - In some meteorites, from 8 to 8 pc associated with 2 to 1 pc of Co. In the sun's atmosphere (Cornu, O. R. 86, 983) Ni has been found, to the extent of 75 pc, in a Pt ore from the Ural (Terreil, O. R. 82, 1116) Chiefly as copper-nickel NiAs, whate nickel NiAs, and Mg-Ni silicate, garmierite. Ni antimonide, arsenate, oxide, sulphide, carbonate, &c., also occur, chiefly in combination with com-

pounds of Co, Fe, Sb, and Bi Ni compounds are always present in Co ores, and Co is almost invariably a constituent of Ni ores Ni compounds have been known to the Chinese for cen turies, Ni forms a constituent of Chinese armour Copper nickel was known to the German miners in the Middle Ages, having in vain attempted to extract Cu from this mineral, they gave it the name of kupfer nickel, or false copper In 1751 Cronstedt showed the mineral to contain a special metal, to which he gave the name of The metal was obtained in impure connickel dition by Cronstedt, and examined by Bergmann, Richter, and others Fleitmann prepared larger quantities of Ni, and applied it to coat iron and Bottger, c 1840, introduced the practice of electro nickel plating, this application of Ni has become an important trade since c 1869

Formation — Copper nuckel, or speiss (a byproduct in the production of smalt), is powdered and roasted (to remove As and oxidise Ni), again roasted with charcoal, dissolved in HNO₂Aq, saturated with H₂S, and the filtrate is ppd by Na₂CO₃, the Ni is separated from the Fe and Co in the pp by different processes (ν Preparation), the Ni is ppd by alkali as NiO xH₂O, the pp is dehydrated by heat, and reduced by C or in H An ammoniacal solution of Ni NH₄ sulphate is sometimes decomposed by electrolysis

Preparation - A salt of Ni, tolerably free from Co, is obtained by such a method as the following from arsenical Ni sulphide, or speiss, speiss is a deposit formed in the pots in which roasted Co arsenide, mixed with copper nickel, is fused with K₂CO₃ and quartz, in the prepara The roasted ore, or speiss, is tion of smalt fused with chalk and fluorspar, the slag being poured off, the metal is powdered and roasted for a long time in a reverberatory furnace till fumes of As2O3 cease to come off, the product is dissolved in HClAq, the solution is diluted, bleaching powder is added to oxidise the Fe salts, and milk of lime to ppt Fe₂O₂ with As oxide, the filtrate is acidified and ppd by H₂S, the filtrate from this pp is heated with bleaching powder to ppt Co oxide, and the Ni remain ing in solution is ppd as oxide by milk of lime (Louyet, J Ph [3] 15, 204, for other methods v Wagner, Berg und Huttenm Zeit 1870 134, Gilchrist, B 16, 264, Donath, D P J 236, 327, Wöhler, P 6, 227, Cloez, J 1857 619, v also DICTIONARY OF APPLIED CHEMISTRY)

Impure N1 may be purified by dissolving in HClAq with addition of HNO,, evaporating to dryness, dissolving in water, acidulating with HClAq, boiling with excess of NaHSO, (to reduce As,O, to As,O,), saturating the warm liquid with H2S (after SO, is all removed), filtering after 12 hours or so, evaporating the filtrate to dryness, dissolving the residue in water, filtering, treating the filtrate with Cl and then ppg Fe and Co by BaCO, removing excess of Ba by dilute H2SO,Aq, filtering, and ppg N1 as carbonate by Na₂CO₂ (Cloez, J 1857 619) After ppg As, Cu, Sb, Pb, and B1 by H2S, the filtrate may be much concentrated and N1 ppd. as oxalate, by addition of oxalic acid (Deville, A Ch [3] 46, 82) Winkler (Fr 6, 18) boils a solution of commercial N1CO, with NaClO till all Co is ppd, this occurs only when a large quantity of N1 is also thrown down; be filters, ppts. by H2S, boils the filtrate, and

ppts NiCO, by addition of Na₂CO, Co is the most difficult impurity to separate from Ni salts; the most effectual method is to dissolve in HNO₂Aq, concentrate, neutralise by KOHAq, mix with KNO₂Aq, strongly acidify with acetic acid, and allow to stand for a few days, when the Co is completely ppd as Co K nitrite, and the filtrate contains the Ni (cf. Zimmermann, A. 232, 324)

Ni is obtained from NiCO₂ (or NiO H₂O ppd from solutions by KOHAq) by washing thoroughly, spreading out to dry, heating till CO₂ is all removed, and then reducing by H, at c 270 (Müller, P 136, 51), or by heating with C, the latter method is conducted by making the NiO into a paste with oil, placing this in a crucible lined with charcoal, and heating in a powerful air- or blast furnace

NiCO₃ may be dissolved in HClAq, the solution evaporated to dryness, the residue of NiCl₂ thoroughly dehydrated, then sublimed in a porcelain tube in a stream of Cl, and finally reduced by heating in H (Winkler, Fr 6, 18)

NiC.O. yields Ni when heated out of contact with air, this may be done by heating under a layer of pounded glass which does not contain any heavy metal

Nis also obtained by electrolysing solutions of its salts, using a weak current, the best solution to use seems to be an ammoniscal one of Ni NH, sulphate (v Becquerel, C R 55, 18, cf Zimmermann, A 232, 324)

Properties -A very lustrous metal, white, with a slight greyish yellow tinge Hard, easily polished, ductile, malleable, and very tenacious. By heating in a poicelain oven, crystals of Ni, apparently regular, have been obtained Slightly magnetic, but less so than Fe or Co Ni obtained by reduction of NiO by charcoal usually contains a little C, such C-containing Ni is softer and less malleable than the purer metal (Boussingault, Chem Ind 1878 130) As obtained by reducing NiO by H, or by heating NiC,O,, Ni forms a greyish black, somewhat porous, pyro-phoric powder As obtained by reducing NiCl in H, the metal forms a compact sponge, and also lustrous leaflets (Winkler, Fr 6, 18, Gard, J 1877 266) By electrolysis of Ni solutions by a very weak current, Ni is obtained as coherent, lustrous, white plates (Becquerel, C. R. 55, 18) After fusion of large quantities of Ni. the metal becomes porous and crystalline, and loses its ductility, this is probably due to absorption of gases, and may be prevented by adding $\frac{1}{8}$ p c of Mg (Fleitmann, B 12, 454)

N1 shows passivity, ie under certain conditions it is unacted on by HNO,Aq According to Saint-Edme (C R 106, 1079), commercial sheet N1 is passive in ordinary HNO,Aq, and passive N1 remains passive when heated to bright redness in H, whereas Fe loses its passivity (cf. Passivity of iron, under Ison, this vol p 52)

Ni is a metallic element. The oxides are basic, or react as peroxides. NiO forms a series of corresponding salts, Ni₂O₂ probably forms salts by reacting with acids, but these salts are reduced very easily to salts of NiO. Ni is closely related in its chemical properties to Co, it is classed with Co and Fe, and also shows analogies with Mn, v IRON GROUP OF HARMENTS, this vol. p. 65. No Ni salts are known correspond-

KK2

ing with the cobalto and cobalti-cyanides, M.CoCy, and M.CoCy, , nor are nickel-ammoniobases known analogous with the cobaltamines, although some N1 compounds, eg the haloid compounds, combine with NH₃ The ultraviolet spectra of Ni and Co do not exhibit much analogy (v. Liveing a Dewar, Pr 43, 430)

The at w of N1 has been determined (1) by reducing NiO in H (Brdmann a Marchand, A 82, 76, Russell, C J [2] 1, 51), (2) by analysing Ni oxalate (Schneider, P 101, 387, 107, 605, 130, 303), by determining Cl in NiCl, (Dumas, A Ch [3] 55, 149), (3) by ppg NiSO, Aq by BaCl, Aq (Sommaruga, W A B 54 [2] 57), (4) by the reaction of AuCl, Aq on Ni, and determining the Au and (Wheller & 6, 22 cr mining the Au ppd (Winkler, Fr 6, 22, cf Kruss a Schmidt, B 22, 11, but v also Winkler, B 22, 890), (5) by decomposing by heat strychnine Ni cyanide and brucine Ni cyanide (Lee, C N 24, 237), (6) by dissolving Ni in HClAq, and measuring H evolved (Russell, C J [2] 7, 294), (7) by determining SH of Ni, the result obtained shows that 58 6, and not a multiple of this number, is the at w, this result has been confirmed recently, (8) by determining V D of gaseous Ni(CO)₄ (Mond, Langer, a Quincke, C J

Alleged decomposition of nickel—Kruss a Schmidt (B 22, 11) found that by repeatedly treating NiS, prepared from the ordinary sulphate, with NH, sulphide, until the latter was no longer coloured brown, a bright yellow residue was ob tained, from this residue they prepared various salts, which they regarded as compounds of a new metal, and finally they obtained the supposed new metal by electrolysing an aqueous solution of the chloride, and also by reducing the dichloride in H Kruss a Schmidt (B 22, 2026) prepared what they considered to be pure Ni, and by fractionally ppg this as basic Ni NH, arsenite they obtained two different substances, one having an at w 56-58, and the other an at w 61-100, hence they concluded that their former results were confirmed, that is, that N1 is really a compound or a mixture of two Considerable doubt was thrown on these results by the work of Winkler on the reaction between pure AuCl, and Ni (B 22, 890), and Fleitmann's experiments on large quantities of Ni also tend to show that Ni has not been separated into unlike parts (Chem Zeitung, 18, 757)

Reactions and Combinations -1 Pieces of Ni do not oxidise in ordinary air, heated in air Ni is superficially oxidised to NiO, Ni obtained by reduction of NiO at low temperatures is pyrophoric -2 Ni burns to NiO when heated in oxygen -8 By heating in chlorine, bromine, or todine, NiOl₂, NiBr₂, or NiI₂ is produced -4 Heated with sulphur, NiS is formed -5 Ni combines with *phosphorus* when the elements are heated together —6 Combines with arsenic in several proportions (v Nickel, arsenides of, p 501) -7 Absorbs, and probably also combines with, carbon (v Nickel, carbides of, p 501) — 8 Combines with carbon monoxide (v Nickel carbon-oxide, p 501) — 9 By reducing NiO in presence of SiO₂, N₁ is obtained, containing silrcon (v Nuckel, silicides of, p 503)—10
Steam is slowly decomposed by N₁ at red heat. NiO being formed (Regnault, A Ch. [8] 62, 852)

11 Netric acid forms Ni(NO₃)₂, but Ni is passive in cone HNO₃Aq —12 Sulphuric and hydrochloric acids react very slowly with Ni (v Tissier, C R 50, 106) -13 Aqueous sulphurous acid is decomposed by Ni at c 200°, with production of Ni₂S₄ (Geitner, A 139, 354) —14 Carbon dioxide is reduced to CO by heating with Ni to redness (Bell, C N 23, 358)—15 Heated in carbon monoxide to 850°-450°, C is deposited and CO, produced (v supra, No 8, also Nuckel carbon-oxide, p 501) —16 Forms alloys with several metals (v Nickel, alloys of, infra) — 17 Occludes about 165 times its volume of hy drogen (Raoult, C R 69, 826)

Detection and Estimation -Ni compounds give a bead with borax which is violet when hot and reddish brown when cold in the oxidising flame, and in the reducing flame becomes opaque and grey from reduced Ni Brown black NiS is ppd by alkalı sulphides, insol dilute cold HClAq, somewhat sol yellow NH, sulphide, H₂S produces no pp in acid solutions, moist NiS ppd from cold solutions, oxidises rather easily in the air Very small traces of Ni may be detected, in the absence of most other metals, by the rose-red colour produced by adding K_2CS_3Aq (Braun, J 1868 376) To detect small quantities of Ni in presence of Co, Papasogli places a piece of Zn in a solution of the double cyanides of the two metals if Ni is present a red colour is produced (J 1879 1055), Donath a Mayrhofer ($\tilde{F}r$ 20, 379) add excess of NaOHAq then I, boil, treat the pp with NH, Aq and NH₄ClAq, and test the solution by NH₄HS (v also Jorisson, Fr 21, 208)

Ni may be estimated as NiO after ppn as NiO xH2O by addition of KOHAq to a hot solu tion For separation of Ni from Co v Cobalt, vol 11 p 218 Classen recommends the ppn of N1 as oxalate, which on heating out of con tact with air gives NiO (Fr 16, 471, 18, 189, 386) Ni may also be estimated by electrolysing a solution of Ni NH, oxalate in presence of excess of NH oxalate (v Classen, for description of apparatus v Dittmar's Exercises in Quanti tative Chemical Analysis [Glasgow, 1887], cf Merrick, C N 24, 100)

Technical Applications -Alloys of Ni with Cu, and with Cu and Zn, are used for coinage in some countries, and for other purposes These alloys are nearly white and hard articles of iron and steel are now covered with a deposit of Ni This covering is only very slightly acted on by ordinary air Nickel plating is usually accomplished by electrolysing an ammoniacal solution of Ni NH, sulphate, using Ni as one of the electrodes, and the substance to be plated as the other (v D P J 201, 145, 206,288, 211, 74, 212, 160, 219, 469, v also Adams, C R 70, 123, 137, Becquerel, ibid 70, 124, 137, 181, v also DICTIONARY OF APPLIED CHEMISTRY)

An alloy of N1 with Nickel, alloys of aluminium, approximately Al, Ni, is obtained by melting together 8 parts Al with 8 parts dry NiCl, and 20 parts mixed KCl and NaCl, and treating with dilute HClAq (Michel, A 115, 102) Alloys of Ni with copper, and with copper and sunc, are used for coinage and other purposes under the names of German silver, packfong, &c Ramsay (C. J 55, 582) found that an amalgam-

of Ni with mercury could be obtained in small quantities by electrolysing dilute solutions of Ni salts in contact with Hg

Nickel, ammonio-compounds of Some Ni compounds, eg NiCl, and NiBr, combine with NH, v Nickel bromide, Nickel chloride, &c

Nickel, antimonates of, N1(SbO₂)₂ 6H₂O and N1(SbO₂)₂.12H₂O, v Heffter, P 86,446

Nickel, antimonide of NiSb occurs native as breathauptite

Niekel, arsenates of, v vol 1 N13(AsO4)2-8H2O occurs native as nickel bloom

Nickel, arsenides of A brittle compound Ni2As, is formed by heating Ni with excess of As, also by very strongly heating Ni arsenates In a charcoal-lined crucible (For other arsenides v Descamps, C R 86, 1065) Various Ni ores are essentially compounds of N1 and As, N1,As, = speiss, NiAs = copper-nickel, NiAs = whitenickel

Nickel, arsenite of, v vol 1 p 306

Nickel, borate of, v vol 1 p 530

Nickel, borate of, NiBr₂ This, the only compound of N1 with Br, is obtained by passing Br vapour over finely divided Ni heated to low redness NiBr₂ forms a brownish-yellow solid, it sublimes in yellow, glittering scales (Berthemot, A Ch [3] 44, 389, Rammelsberg, P 55, 243) Heated in air, or in steam, NiBr, forms NiO, it is completely decomposed by HNO,Aq Soluble alcohol and ether, deliquescent, soluble water to a green liquid

The hydrate NiBr, 3H,O is obtained, in green needles, by digesting Ni with BrAq, also by dissolving NiO or NiCO, in HBrAq, and evaporating (Rammelsberg, P 55, 243) This hydrate HF [N1, Br2, Aq] is dehydrated at c 200° =71,820 (Th 3,307)

A compound of nickel bromide with ammonia, NiBr₂ 6NH₃, is obtained as a violet powder, by passing NH₂ over powdered NiBr₂, also, as a blue powder, by warming cone NiBr2Aq with excess of NH₂Aq, and cooling NH₂ is given off when the compound is heated NiBr₂ 6NH₂ is soluble in a little water without decomposition, much water causes ppn of NiO.H.O (Rammelsberg, lo)

Nickel, carbides of Commercial Ni always contains a little C For experiments on carbonisation of Ni v Gard, Am S [3] 14, 274, Boussingault, C R 86, 509, Pebal, A 233, 160, Gautier a Hallopeau, C R 108, 1111, Mond,

Langer, a Quincke, C J 57, 749

Nickel carbon-oxide Ni(CO), Mond, Langer, a Quincke (C J 57, 749) found that Ni decomposes CO at 850°-450°, with separation of C and formation of CO₂. When the product was formation of CO₂. When the product was allowed to cool in CO they noticed that the escaping gas caused a Bunsen flame to become very luminous, and when heated deposited Ni Following up this observation they found that when finely divided Ni, produced by reducing the oxide in H, is allowed to cool in a slow current of CO the gas is readily absorbed by the Ni when the temperature has fallen to c 100°, and that by replacing the CO by CO₂, N, H, or ar, a mixture of gases is obtained which deposits Ni when heated above 150° By analysing the mixture of gases thus obtained, and determining the Ni by passing the gases through a capillary tube at 180°, M, L, a. Q found that one volume of

the N1 compound present in the gases gave four volumes of CO. The analyses led to the formula NiC,O, By passing the mixed gases through a tube surrounded with salt and ice a colourless mobile liquid was obtained, which was proved, by estimations of Ni and C, to be NiC,O, The V.D determined at 50° was found to be 869, NiC4O requires 804 The new compound is called nickel carbon-oxide by its discoverers, it boils at 43° at 751 mm, solidifies at -25° to needleshaped crystals, and has S G 1 3185 at 17°. The vapour is very poisonous The compound is sol. alcohol, benzene, and chloroform, it is not acted on by dilute acids or alkalis, nor by conc HClAq; cone HNO, Aq and aqua regra dissolve it readily. The vapour ppts Ag from AgCl in NH,Aq, it is decomposed by Cl, giving NiCl, and COCl, Bracts similarly, electric sparks produce Ni and CO

Nickel, chloride of, NiCl, H F. [Ni,Cl²] = 74,530 (Th 3,307), [NiCl²,Aq] = 19,170 S G 2 56 (Schiff, A 108, 21) Prepared by gently N1Cl2 heating powdered Ni in a stream of dry Cl, and subliming in the Cl (H Rose, P 20, 156) by dissolving NiO or NiCO, in HClAq, or Ni in aqua regia, and evaporating to dryness Golden yellow scales Sublimes readily without melt-Prepared in the wet way, NiCl, is deliquescent and easily soluble in water, sublimed NiCl, dissolves slowly in boiling water Heated in air Cl is evolved and NiO formed Heated in a stream of O, is entirely changed to Ni₂O₄ (Schulze, J pr [2] 21, 407) KOHAq decomposes sublimed NiCl, only after prolonged boiling PH, forms Ni,P, and HCl, molten P forms Ni,P, and PCl, (H Rose, P 27, 117) For ing S G of cone NiCl, Aq v Franz, J pr [2] 5, 274

The hexa hydrate NiCl, 6H,O (Laurent

(Laurent, A Ch [3] 60, 354) is obtained by cooling conc NiCl₂Aq Soluble in $1\frac{1}{2}$ -2 parts water, sol in alcohol Sabatier (Bl [3] 1, 88) describes a dihydrate NiCl₂2H₂O, obtained by placing the hexahydrate over H2SO, in vacuo at 20° for three months Thomsen gives [Ni, Cl², $6H^2O$] = 94,860 (Th 8, 807)

The oxychloride NiCl, 8NiO 13H, O is obtained by adding a little NH, Aq to NiCl, Aq (Raoult,

C R 69, 826)

Compounds with ammonia (1) NiCl. 6NH. is obtained by passing NH, over dry NiCl, (H. Rose, P. 20, 155), also by adding alcohol to NiCl, in NH.Aq (Erdmann, Gm-K (6th edit) 3, 553, F Rose, Gm K (6th edit) 8, 561). Soluble without change in cold water, decomposed slowly by much cold water, quickly by hot water Slightly sol cone NH,Aq, insol alcohol.
(2) NiCl, 2NH,, obtained by heating NiCl,6NH, to 120° Gives NiCl, when heated in vacuo, and a little Ni when very strongly heated

Compounds with ammonium chloride NiCl. NH Cl 6H2O, green deliquescent crystals, obtained by evaporating a solution of the constituents in the ratio NiCl, NH, Cl (Hantz, A. 66, 283) Jörgensen (Gm.-K (6th edit) 8, 561) obtained crystals containing c 5 pc. NiCl, by evaporating NiCl_Aq with a large excess of NH₄Cl (2) NiCl_4NH₄Cl.7H₂O, yellow, star-shaped, crystals, obtained by decomposing Ni-NH₄ sulphate solution by an equivalent of BaCl, filtering and evaporating over H SO, (Adams a Meyrick, J 1871 308, cf Tupputi, A. Ch [3] 78, 169)

NiCl, form double salts with CsCl, CdCl, and

AuCl. (v Goddefroy, B 8, 9, von Hauer, W A B 20, 40; ibid W A. B 17, 848)

Nickel, chromates of, v. vol 11 p 156 Nickel, cyanide and double cyanides of, v.

vol 11. p 848
Nickel, ferricyanide of, v vol 11 p 839 Nickel, ferrocyanides of, v vol 11 p 336

Nickel, fluoride of, NiF₂ S G 2 855 at 14° (Clarke, Am S [3] 13, 291) The hydrate NiF₂8H₂O is obtained by dissolving NiO H₂O or NiCO, in HFAq, and evaporating (Berzelius, Clarke, Am S [3] 13, 291) Decomposed by much hot water to oxyfluoride Ni₂OF₂ H₂O (Berzelius) Combines with AlF₃, fluorides of the alkalı metals (Wagner, B 19, 896), and with SiF₄ (v. Nickel, silicoftuoride of, p. 503), TiF₄ (v. TITANIUM FLUORIDE), and ZiF₄ (v. Zirconium FLUORIDE) With Mo₂O₂F₂ forms the compound NiF₂MoO₂F₂6H₂O (Delafontaine, J. 1867, 236) Nickel, hydroxides or hydrated oxides of, v

Nickel, oxides and hydrated oxides of, infra Nickel, iodide of, NiI₂ [Ni, I², Aq] = 41,400 (Th 8, 307) Prepared by heating Ni, reduced from NiO by H, with I, and subliming the NiI, from the residue of N1 and N1O (Erdmann, J pr 7,249) Also by heating N1I, 6H,O, which is obtained by dissolving N1O H,O in HIAq, or by treating finely divided Ni with excess of I and water Iron black, lustrous, metal like, scales Deliquescent, soluble in water, forming a brown liquid, which becomes green on dilution Partly decomposed when strongly heated in air By digesting NiLAq with NiO H₂O, or by evaporating NiI₂Aq, Erdmann (lc) obtained the oxyrodide NiI₂9NiO 15H₂O

Compounds with ammonia (1) NiI₂ 4NH₃, a yellow-white mass, by passing NH, over NiI, (Rammelsberg, P 48, 119) (2) NiI, 6NH, by adding excess of NH, Aq to cone NiI, Aq, warming, and cooling or adding alcohol (Erd-

mann, lc, Rammelsberg, lc)
Nickel, nitride of A compound of Ni with N is said to be formed by heating NiO to c 200° in NH, it is decomposed at a higher tempera-

ture (Warren, C N 55, 155)

Nickel, oxides and hydrated oxides of Nickel forms three oxides, NiO, Ni₂O, and Ni₂O₃, a fourth oxide, Ni₂O, probably exists, there are indications of the existence of oxides intermediate between Ni₃O₄ and Ni₂O₅, and also of an oxide containing more O than Ni₂O₃ Hydrates of NiO and Ni₂O₃, and perhaps of Ni₂O₄, have been isolated The oxides of Ni are basic, but the only N1 salts which have been prepared with certainty correspond with NiO NiO is oxidised by heating to c 400°, but the product is reduced to NiO at c 600°

NICKEL MONOXIDE NIO (Nickelous oxide Protoxide of nickel) Occurs native as bunsenite Obtained by heating N1 or N1Cl, in steam (Regnault, A Ch [3] 62, 352), by heating the hydrate or NiCO_s in absence of air, by strongly heating Ni(NO₂)₂ (Russell, C J [2] 1, 58), NiSO₄ (Baubigny, C R 97, 951), or a mixture of NiSO, and K.SO. (Debray, C R 52, 985), by reducing NiO, by H at 190°-280° (Moissan, A Ch [5] 21, 288, cf Wright a Luff, C. J 88, 1, also Müller, P 136, 59), or by NH, at c 180° (Vorster December 1981) (Vorster, Dessertation, Göttingen, 1861), at a moderate temperature NiO is obtained in green regular octahedra by heating Ni borate with CaO

in a porcelain oven, and treating the product with HClAq (Ebelmen, C R 33, 526)

526) Heated to 350°-440°, NiO is oxidised to N₁O₂, which is again deoxidised to NiO at c 600° (Moissan, A Ch [5] 21, 199) NiO is readily reduced to Ni, reduction by CO begins at c 120°, by H at c 220°, by O at c 450° (Wright a Luff, C J 33, 1), reduction by NH, begins at c 200° (Vorster, Dissertation, Göttingen, 1861) NiO is oxidised to Ni₂O, by ozonised O (Schonbein, J pr 93, 35) NiO, if not strongly heated, dissolves in NH_2Aq , it decomposes NH_4 salts with evolution of NH_2 NiO dissolves in acids forming salts NiX_2 , $X = NO_3$, ClO_3 , $\frac{1}{2}SO_4$, $\frac{1}{3}PO_4$,

HYDRATE OF NICKEL MONOXIDE 4N1O 5H,O = 4N1(OH), H₂O (Nuckelous hydrate, nuckelous hydroxide) This hydrate is obtained as a pale greenish pp, by adding alkalisolution to solution of a Ni salt According to Teichmann (A 156, 17) the hydrate can be obtained free from acid only from N1(NO₃)2Aq, T recommends to add NaOHAq, free from carbonate, to cold N1(NO₃)₂Aq, to wash the excess of pp with cold water till the alkaline reaction disappears, then to wash with water containing a little NH₂, and finally with boiling water, and to dry at 100° 4N1O 5H2O 18 also obtained, as a green crystalline powder, by heating NiO or NiCO, in NH, Aq (Gm K (6th edit) 3, 536)

Nickelous hydrate is a pale green powder, slightly soluble in water (Fresenius) If not washed free from alkalı it oxidises in presence of air and SO, Aq, but the product is reduced to NiO by excess of SO₂Aq (Wicke, Z 1865 86) When strongly heated, H₂O is evolved and NiO remains H₂O₂Aq forms a hydrate of Ni₂O₄ (Schönbein, J pr 93, 35), but, according to Bayley, H₂O.Aq is without action (P M [5] 7, 126) Oxidised by Cl and hypochlorites to Soluble in NH3Aq and solutions of $N_{12}O_8 xH_2O$ NH_3 salts NH_3 and solutions of NH_4 salts NH_3 and solutions of NH_4 salts NH_4 salts NH_4 and solutions of NH_4 salts NH_4 and solutions of NH_4 salts NH_4 and NH_4 salts NH_4 and NH_4 salts NH_4 and NH_4 salts NH_4 salts NH_4 and NH_4 salts NH_4 and NH_4 salts NH_4 sa 8, 307)

NICKEL SESQUIOXIDE N12O2 (Nickelic oxide Sometimes called nickel peroxide) A black powder, SG 484 at 16° (Herapath, P M 64, Obtained by decomposing by heat at the lowest possible temperature Ni(N₂)₂ (Berze lius, Vorster, Dissertation, Göttingen, 1861), or Ni(ClO₂)₂ (Wachter, J pr 30, 327), also by melting NiCl₂ with KClO₂ (Schulze, J pr [2] 21, 407), also by treating Ni salts in solution with 931) Heated in air to 6 600° Ni₂O₄ is reduced to NiO (Moissan, A Ch [5] 21, 199), reduction in H begins at c 190° (M, lc) Dissolves in H2SO Aq or HNO Aq with evolution of O, in HClAq with evolution of Cl, in each case salts of NiO are produced. Soluble in NH₂Aq with evolution of N (Müller, P 186, 59)

HYDRATES OF NICKEL SESQUIOXIDE. (1) N1,O, 2H,O; brownish crust, S G 2 744, obtained by electrolysing an alkaline solution of

Ni K tartrate (Wachter, J pr 80, 827) (2) $N_{12}O_{13}3H_{2}O_{13}$, by oxidising $N_{11}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{13}O_{$ suspended in water, by Cl or BrAq, also by add ing alkalı and NaClO to solution of a Ni salt (Wachter, Ic) A black solid, which reacts with acids and NH₃Aq as Ni₂O₃ does, reduced to 4N10 5H₂O by SO₂Aq (Wicke, Z 1865 86), also by Na₂SO₂Aq (Schulze, J 1864 270) H F [Ni²,O³,3H²O] = 120,380 (Th 3,307) Carnelley a Walker (C J 53,91) think that no definite stable hydrate of Ni₂O, exists

NICKELO NICKELIC OXIDE NI,O, A grey, metal like, non magnetic solid, obtained by passing O over NiCl₂ at 350°-440° (Baubigny, C R

87, 1082)

NICKELO NICKELIC HYDRATE A black powder, having the composition Ni₈O, H₂O $(=N_{12}O_3 6N_1O H_2O)$, is said to be formed by

heating NiCO₃ to 300° (H Rose, P 84, 571) NICKEL SUBOXIDE An oxide, Ni₂O, is said to be produced by reducing NiO in H at 210°-214° (Muller, P 136, 59), also by reducing NiO in CO at a low temperature (Bell, C N 23, 258, 267)

NICKEL PEROXIDE By the reaction of hypo chlorites on Ni₂O₂ 3H O one or more oxides are produced containing more O than Ni₂O₃ Wicke gives the composition Ni_4O_7 (Z 1865 303), Bayley (C N 39, 81) gives the formula Ni, O, Carnot (C R 108, 610) says that Ni salt solutions give Ni₂O₃ when treated with hypochlorites or with Br and KOHAq

Nickel, oxychloride of, v Nickel chloride, p 501

Nickel, exyfluoride of, v Nickel fluoride, p 502

Nickel, oxyiodide of, v Nickel wodide, p 502

Nickel, phosphides of Ni and P combine when heated together Various compounds have been described (1) N₁,P₂, by heating N₁, bone ash, quartz sand, and C (Gm K (6th ed.) 3, (Struve, J. 1860. 76) (3) N₁₂P₂, by reducing 5NiO P₂O₃ in H (Struve, J. 1860. 76) (3) N₁₃P₂, by reducing 3NiO P₂O₃ in H (H. Rose, P. 24. 332), also by heating NiCl₂ or NiS in PH₃, or by passing PH₃ over heated Ni (Davy, Schrotter, W. A. B. 2, 204). 304)

Nickel, salts of Compounds obtained by replacing H of acids by Ni The Ni salts which have been studied all correspond with the oxide N₁O, and belong to the form N₁X₂ where $X = ClO_3$, NO₃, $\frac{1}{3}SO_4$, $\frac{1}{6}CO_3$, $\frac{1}{3}PO_4$, &c The oxide N₁O₃ probably forms salts, but they are very easily reduced to salts of N₁O. The N₁ salts are obtained by dissolving Ni, NiO, or NiCO, in acids salts of N1 are generally yellowish when dehydrated, and green when combined with water Some of the compounds of Ni combine with The haloid compounds, the sulphate and nitrate of Ni, and some of the other salts, are soluble in water, the oxides, sulphides, phos phate, carbonate, and a few other salts, are insoluble in water Solutions of Ni salts in water are green, they redden litmus slightly Ni salts are decomposed by heating in air, N₁Cl₂, N₁Br₂, and N₁I₂ can be sublimed unchanged The chief Ni salts of oxyacids are the antimonate, arsenates and -ite, borate, bromate, carbonate, chlorate, chromate, sodate and persodate, molybdates, nitrates and -ste, phosphates and its and hypophosphite, selenate, silicates, sulphates

and -ite, thiosulphate (v Carbonates, Nitrates,

&c)
Nickel, selenide of, NiSe A silver white, brittle, crystalline, solid, SG 846, obtained by action of Se vapour on finely powdered Ni Melts at red heat, with loss of Se Insoluble in HClAq, slowly dissolved by HNO, Aq, quickly by aqua regra (Little, A 112, 211)
Nickel, silicides of Commercial Nigenerally

contains more or less Si For experiments on the quantity of Si taken up by Niv Gard, Am S

[3] 14, 274 Nickel, silicofluoride of, NiSiF, 6H,O Hexagonal rhombohedral, green crystals, SG. 2109, by dissolving NiCO, in H₂SiF₂Aq De composed at red heat, giving NiF₂ and SiF₄ (Berzelius, Marignac, Ann M [5] 15, 262)

Nickel, sulphides of Four sulphides of Ni are known Ni,S, NiS, Ni,S,, and NiS, N1S 18 somewhat soluble in NH, sulphide, it also forms a compound with K2S. The only sulphide pro duced by the direct union of Ni and S is NiS

NICKEL MONOSULPHIDE NIS Occurs native as capillary pyrites or millerite Formed by heating Ni with S, by heating NiO with S, or in a stream of H.S (Tupputi, A Ch [3] 78, 133, 79, 153), also by heating NiCl, with K₂SAq in a sealed tube to c 160° (Sénarmont, A Ch [3] 30, 142) As prepared by these methods, NiS is a yellow, brittle, solid, decomposed very slowly by steam at red heat (Regnault, A Ch [3] 62, 280), not decomposed by H, slowly acted on by Cl when hot (v P 42, 540), oxidised by heating in air, acted on by PH,, when hot, with formation of $\mathrm{Ni}_2\mathrm{P}_2$ (Schrötter, W A B 2, 304), insol HClAq, sol HNO₃Aq and aqua regia

NiS, in combination with water, is ppd from neutral N₁ solutions by H₂S, or by NH₄HSAq, also by heating N₁ salts with Na₂S₂O₃Aq prefer ably in sealed tubes at c 120° (Gibbs, Am S [2] 37, 346) Thomsen gives [Ni,S, $nH^{2}O$] = 19,400 (Th 3, 307)The pp thus obtained is brown black, if ppd from boiling solutions it may be washed and dried without change, but if ppd from cold solutions it oxidises in the air (Clermont a Guiot, C R 84, 714, 85, 73) Decomposed by Guiot, C R 84, 714, 85, 73) Decomposed by boiling with water (Geitner, A 139, 354) Some what soluble in NH, Aq and alkalı sulphide solu tions, the brown solutions thus obtained deposit NiS by standing in air or on addition of a weak According to Baubigny (C R 94, 1417) the pp produced by H,S in neutral solutions of Ni salts is a hydrosulphide which is decomposed to NiS and H₂S by filtration A very dilute aqueous solution of a colloidal form of NiS was obtained by Winssinger (Bl [2] 49, 452) by ppg from a very dilute solution and dialysing

Compound with potassium sulphide, 3NiS K2S A yellow, lustrous, crystalline solid, obtained

by fusing NiSO, with K2CO,

NICKEL DISULPHIDE NIS. A dark fron grey powder, obtained by strongly heating NiCO. with K2CO3 and S, and treating with water (Fel-

lenberg, P 50, 75)

NICKELO NICKELIC SULPHIDE NIS An amorphous greyish-black solid of this composition is obtained by heating NiCl.Aq with polysulphides of K to 160° (Sénarmont, A Ch [3] 80,142), by heating Ni with SO.Aq or Na.SO.Aq to 200°, Ni S, is obtained in rhombohedral crystals (Gestner. A 189, 354)

NICKEL SUBSULPHIDE NLS A yellow, metallike solid, obtained by heating NiSO, to redness, also by heating NiSO₄ or ppd NiS with S in H (H Rose, P 110, 31) Ni₂S was obtained in small crystals by heating Ni in CS₂ vapour to bright redness (Gautier a Hallopeau, C R 108, 1111) Prolonged heating in CS, produces NiS

Nickel, sulphocyanide of, v vol 11 p 850

M M P M

MICOTIANIC ACID v Pyridine Carboxylic

NICOTINE C10H14N2 16

OH CH CH CH CH CH2 CH2 CH2 N (?) OF CH CH C CHEt CH (Pinner, B 24, 61) pyridyl hexahydride (Liebrecht, B 19, 2587) Mol w 162 (247° cor) at 745 mm S G 4 1-0183, \$\frac{9}{2}\$ 1 0110 (Landolt, \$A\$ 189, 318) ۷Ď 5 61 (calc 5 58 (Barral, J 1847, 614) SH 420 (Colson, Bl [3] 3, 8) Heat of solution and of neutralisation (Colson, A Ch [6] 19, 407)
[a]₀ = -161 6° (L)

Occurrence -In leaves of tobacco (Nicotiana Tabacum) (Vauquelin, Posselt a Reimann, B J 10, 198), and in the leaves of Macrophylla rustica and M glutinosa Occurs also in Pituri (Gerard, J 1878, 915, Petit, J 1879, 791) cording to Zeise and to Vohl and Eulenberg (Ar Ph [2] 147, 130) it is not present in tobacco smoke, but Heubel obtained evidence of its pre-

sence therein (D P J 207, 343)

Preparation -Tobacco leaves (10 pts) are soaked in water for 24 hours, and the mixture heated to 100° by steam. The aqueous extract is mixed with lime (1 pt) and distilled. The distillate is neutralised by oxalic acid and evaporated to a thin syrup Addition of cone KOHAq now separates the base, which is rec tified in a current of H (Laiblin, A 196, 130)

Properties - Colourless liquid, not frozen at Smells like tobacco, unless it is quite pure It is very hygroscopic Mixes with water, developing heat Leevorotatory The optical activity of its aqueous solution varies greatly with concentration in a 4 p c solution $[a]_D = -77^{\circ}$ at 20°, in a 88 p c solution $[a]_{\rm D} = -79^{\circ}$ (Pribram, B 20, 1840) Solutions of salts of nicotine are dextrorotatory Nicotine has a burning taste and is very poisonous. Nicotine turns brown on exposure to air and light. Its solutions are strongly alkaline. It is very soluble in water, alcohol, ether, terpenes, and fatty oils 100° it dissolves 10 pc of sulphur Ether extracts it from the aqueous solution KOH separates it from aqueous solution

Estimation —1 By distilling with potash,

extracting the distillation with ether, evapora ting the ether, converting the residue into sulphate and repeating the process -2 Tobacco is mixed with aqueous NaOH and some alcohol and extracted with ether The extract is eva porated and the nicotine distilled over with steam and estimated by titration with standard acid, or by the polarimeter (Kissling, Fr 21, 75, 22, 199, Ohem Zett 13, 1030, Popovici, H 13, 445; Biel, Ar Ph [3] 26, 322)

Reactions.—1 Oxidised by intric acid, chromic acid mixture, or KMnO, to pyridine

carboxylic (micotinic) acid (Huber, A 141, 271; Laiblin, B 10, 2186) — 2 Alkaline K, FeCy, oxi-

dises it to isodipyridyl (C a E) -8 Nicotine (5 pts) heated with sulphur (1 pt) at 140° gives H_2S and 'thiotetrapyridine' $C_{20}H_{18}N_4S$, which separates from boiling alcohol in sulphur-yellow crystals [155°], and forms the salts B"H₂Ol₂, B"H₂PtCl₄, and B"HHgCl₄. On distillation with finely divided copper, thiotetrapyridine is con verted into isodipyridyl (Cahours a Etard, C R 88, 999, 90, 275) -4 Vapour of nicotine passed through a red hot tube is partly decomposed, yielding paraffins, olefines, pyridine, methylpyridine, and collidine (C a E) -5 Nicotine 5 pts) heated with selenium (1 pt) at 240° forms isodipyridyl and collidine dihydiide C_sH_{1s}N (203°) (Cahours a Etard, C R 92, 1079) —6 Bromine added to a dilute aqueous solution of nicotine forms a yellow flocculent pp If this be dissolved by heating to 70° red crystals of the tetrabromide C10H14N2Br4 separate on cooling With cone HBrAq they form the salt C₁₀H₁₄N₂Br₄HBr (Cahours a Etard, C R 90, 1315) —7 By distilling the double chloride of zinc and nicotine with lime there is formed pyrrole, methylamine, NH, and a liquid base C_{1e}H₁₁N (250°-270°) with disgusting odour solution of the hydrochloride of this base is coloured dark red on boiling with PtCl4 (Laiblin, A 196, 172) -8 Sodium reduces nicotine in alcoholic solution to dipiperidyl —9 HI and P at 260° gives nicotine dihydride.—10 H2O2 in presence of platinum black forms orange granu lar crystals of oxy-mootine C₁₀H₁₄N₂O, which is oxidised by KMnO, to nicotinic acid, and forms a picrate [154°-158°] (Pinner a Wolffenstein, B 24,65)—11 HgO at 240° yields oxytrinicotine C₆₆H₅₄N₁₂O₄ (?) which separates in brown flakes on addition of KOH to its acid solution. Its platmochloride C₆₆H₅₄N₁₂O₄4H₂PtCl₆ 12aq brownish yellow (Etard, C R 97, 1218)

Salts —B"H₂Cl₂ long fibrous deliquescent crystals (Barral, A 44, 281) [a]_D = +102° — B"H_PtCl yellow crystalline pp or ruby red prisms, very soluble in excess of nicotine, insol alcohol and ether Not decomposed by boiling water (O De Coninck, Bl [2] 45, 181)— B"H,PtCl, orange prisms (from HClAq) Ob tained by adding nicotine to a solution of pla tinous chloride in HClAq (Raewsky, J 1847, The mother liquor from which this salt has separated deposits red crystals of B"H_PtCl. -B"2H2SO, crystals, v sol water and alcohol -B"HgCl2 white pp, formed by adding mer-curic chloride to a solution of nicotine Insol water and ether, almost insol alcohol (Ortigosa, A 41, 118) —B"3HgCl₂ Long crystals, de posited on standing by a dilute solution of nico tine hydrochloride to which HgCl2 has been added until a permanent pp begins to form (Boedeker, A 78, 372)—B"HÖl4HgOl2 crystal line pp obtained by adding a cold neutral solu tion of nicotine hydrochloride to a large excess of mercuric chloride —B"H_ZnCl,4aq crystals (from 80 p c alcohol) (Vohl, J pr [2] 2, 331) — B"H_Cl_8n_Cl_aq [162] Crystals, got by B"H₂Cl₂Sn₂Cl₃aq [162²] Grystals, got by adding tin to the hydrochloride (Colson, Bl [3] 8, 11) —B"H₂CdCl₂2aq (V) —B"H₂I₂ needles (Wertheim, J 1863, 441) —B"H₂H₃ colourless crystals (from hot water) —B"H₂H₃ yellow prisms, sol cold water and alcohol —B"ZnI₂—B"H₁ —B"HCl₁H₁ —B"AgNO₂ Prisms—B"GNO₃ Prisms—B"GNO₄ Prisms—B"GNO₅ Pr Tartrate B"(C,H,O,), 2aq. white crystalline NIOBLUM 505

tufts, v sol water (Dreser, Ar Ph [3] 27,266) -Nitroprusside sol water (Davy, Ph [3] 11, 756)—Chloro-1odide, dark-yellow pp (Ditt-mar, B 18, 1612)—Picrate B"2C₄H₂(NO₂)₂OH [218°] Yellow needles (P a W)

Methylo 1odide B"Me₂L₂ (Stahlschmidt, A 90, 222) With most Ag₂O it yields a caustic

base It yields the salts B"Me2PtCl, B"2MeAuCl, and B"Me2Cl24HgCl2 When the methylo-10dide is treated with alcoholic KOH at 45° it gives a ruby red colouration, on addition of acids the colour remains red, and, on pouring into a large quantity of water, shows a green fluorescence (O De Coninck, C R 104, 1374)

Ethylo-rodide B'Et₂I₂ prisms, v sol water, sl sol alcohol and ether (Von Planta a Kekulé, A 87, 2) Yields with Ag₂O a caustic It forms the crystalline salts B"Et, PtCl, and B"2EtAuCl, and amorphous B"Et, Cl, 3HgCl, An alcoholic solution of the ethylo iodide is coloured garnet red, and finally crimson, by heating with addition of potash for 10 hours on a water bath After acidifying and pouring into water the colour is still red (De Coninck, C R 104, 513)

Isoamylo rodide B"2C,H,,I

B'(C,H₁₁)₂PtCl₆ (Stahlschmidt)

Nicotine dihydride C10H16N2 Hydronicotine $8 G = 17 993 \quad [\alpha]_D = -15^{\circ} 40' \text{ in a } 13.7$ p c solution Formed by heating nicotine with fuming HIAq and red phosphorus at 265° for 10 hours (Etard, C R 97, 1218) Liquid, with faint odour, miscible with water, alcohol, and ether Lævorotatory Its hydrochloride is not ppd by HgCl₂—B"H₂PtCl₆aq pale-yellow crystals, v sl sol water

Isonicotine v DIPYRIDYL TETRAHYDRIDE NICOTINIC ACID v PYRIDINE CARBOXYLIC

Homo nicotinic acid v Di METHYL PYRIDINE CARBOXYLIC ACID

NIGRANILINE v ANILINE BLACK

NIGROSINE A name used by Wolff (Chem Ind 2, 290, 319) to denote a blue black substance C₃₆H₂₇N₃, found among the products of the action of arsenic acid on aniline hydrochloride at 230° Its hydrochloride C₃₆H₂ N₃HCl exhibits in solution blood red fluorescence, and is decolourised by reducing agents The name 'nigrosine' has also been applied to indulines, more especially when obtained by the action of nitro benzene on a mixture of pure aniline and aniline hydrochloride

NIOBATES v p 506

NIOBIUM Nb (Columbium) At w 94 Mol w unknown C N 37, 26) S G 706 at 155° (Roscoe,

Occurrence - Niobates occur in a few rare minerals, e g in columbite, tantalite, samarskite, yttro-ulmenite, euxenite, and some varieties of pitch blende Niobates are generally accompanied by tantalates, tungstates, titanates, zirconates, and compounds of Th, Ce, and Yt

History -In 1801, Hatchett found a new oxide in a mineral called columbite from Massachusetts, to the metal of the new oxide he gave the name columbium (Crell's Ann 1, 197, 257, 352) In the following year, Ekeberg (Scher J. 9, 597) examined two minerals—one from Finland, the other from Sweden-and announced the discovery of a new oxide, as the oxide was

soluble only in caustic alkalis and was ppd by acids, Ekeberg gave to the metal of this oxide the name tantalum In 1809, Wollaston (S. 1, 520) pronounced the oxides discovered by Hatchett and Ekeberg, respectively, to be identical. Berzelius confirmed the decision of Wollaston (P 4, 6), he proposed to apply the name tantalum to the characteristic metal of columbite and the minerals examined by Ekeberg Oxide of tantalum was recognised as present in several rare minerals (v Hermann, J pr 38, 91, H Rose, P 63, 321) In 1844, H Rose began a series of researches on the minerals containing tantalum compounds (P vols 63, 69, 73, 74, 90, 99, 100, 101, 102) Rose concluded that oxides of three distinct metals exist in these minerals oxide of tantalum in tantalite from Finland and Sweden, and oxides of two new metals, which he called niobium and pelopium, in tantalite from Massachusetts (formerly called columbite) and in a tantalite from Bavaria 1853, Rose came to the conclusion that the compounds described by him as oxides of niobium and pelopium were really two different oxides of the same metal which was different from tantalum, this metal Rose called niobium (from Niobe, the daughter of Tantalus) (Rose, P 63, 317) As different specimens of niobium oxide showed considerable differences of S G, Marignac re examined the ground, and showed that some of Rose's oxides of niobium contained tantalum (C R 60, 234, 1355) Marignae also showed that the most probable formulæ for the oxide and chloride of Nb are Nb₂O₅ and NbCl₅, respectively Blomstrand (J pr 97, 57) confirmed Marignac's results Determinations of SG of gaseous Nb chloride and oxychloride by Deville a Troost (C R 56, 891) have shown the formulæ NbCl, and NbOCl, to be molecular Rose supposed he had obtained Nb by reducing a compound of Nb, K, and F by Na, Delafontaine showed that Rose's supposed Nb was really NbO, and that the compound from which it was obtained contained O (Ar Sc 27, 167) Blomstrand obtained Nb, containing some H, in 1864 by reducing the chloride in H, in 1878 Roscoe prepared approximately pure Nb by the same method $(C \ N \ 37, 25)$

The existence of three other metals in niobium containing minerals has been asserted by von Kobell (*J pr* 79, 291, 83, 193, 449), and Hermann (*J pr* 88, 91, 119, *J pr* [2] 8, 378; 4, 178, 15, 105), but the researches of Blomstrand and Marignac (lc) make the existence of these metals-diomium, ilmenium, and neptunum-very doubtful

Preparation - Very finely powdered columbite is fused with 3 times its weight of KHSO. in an iron or Pt crucible, until completely dissolved, after cooling, the residue is powdered and treated with boiling water, whereby sulphates of K, Fe, and Mn are removed, the insoluble portion is washed, and digested with yellow NH, sulphide, sulphides of Sn and W thus go into solution and FeS remains mixed with Nb.O and Ta₂O₅, the residue is washed and digested with HClAq, to remove FeS, the insoluble in acid is thoroughly washed with boiling water until white. To separate Nb from this mixture of Nb₂O₅ and Ta₂O₅, the whole is dissolved in HFAq, the solution is heated to boiling, and 506 NIOBIUM

part KHF, is added for each part of mixed | Nb₂O₃ and Ta₂O₃ used, the liquid is evaporated | until 1g of the mixed oxides is present in about 7 cc, and allowed to cool, crystals of K2TaF separate, these are washed with cold water till the washings give no red, but a pure yellow, pp with tincture of galls, the filtrate is concentrated with addition of KHF2, and the second crop of K₂TaF, crystals is removed and washed one or two repetitions of this process, fine tablets of NbOF, 2KF separate on evaporating the filtrate from the K.TaF, crystals, the tablets are col lected, pressed, and heated in a Pt dish with H2SO4 until HF is completely removed, the residue is boiled with a large quantity of water for some time, when a white pp of Nb₂O₅ xH₂O separates out (Berzelius, v also Marignac, Ar Sc 23, 167, 249, 25, 5) The pp of Nb₂O₅ xH₂O is washed, dried, and heated to redness, it is then mixed with a large excess of charcoal, the mixture is heated, then placed in a large hard glass tube (a small quantity being used, as NbCl, is very voluminous), heated in dry CO2 until perfectly dry, and allowed to cool in dry CO₂, the CO₂ is then completely expelled by dry Cl, and the tube is then heated to redness while dry Cl passes through it, NbCl, collects in the tube, and is distilled in a stream of dry Cl The NbCl, is then vapourised in a current of perfeetly dry H, with precautions to prevent the entrance of air and moisture, and the mixed vapour is passed through a red hot tube of hard glass The grey, lustrous crust of Nb which forms in the tube is finally strongly heated in a stream of perfectly dry H (Roscoe, C N 37, 25) Nb thus prepared contains about 27 pc H

Properties and Reactions - A steel grey lustrous metal S G 706 at 155° (Roscoe, Ic) Insol HClAq, HNO, Aq, or aqua regia, sol conc H2SO, Heated in air, burns to Nb2O, Heated

in Cl forms NbCl.

The at w of Nb has been determined (1) by determinations of VD of NbCl, and NbOCl, (Deville a Troost, C R 56, 891, 60, 1221), and by analyses of NbCl₅ (H Rose, P 104, 432, Blomstrand, Acta Univ Lund 1864, Marignac, Bibl Univ Genève, 1865 and 1866), (2) by analyses of NbOF, 2KF aq (Marignac, lc)

Nb is metallic in its physical properties NbO and Nb₂O₅ dissolve in conc H₂SO₄, but no definite sulphates or other salts of the oxides have been isolated Nb₂O₅ xH₂O forms several niobates, in which Nb forms part of the negative Nb forms the third member of the even-series family of Group V , it is closely related to Ta, and less closely to N, P, V, As, Sb, Di, Er, and Bi (v Nithogen Group of Elements, this vol p 571)

Detection and Estimation .- Niobates dissolve in hot HClAq, on adding water and boiling, Nb,0,xH₂O ppts Solutions in HClAq are coloured blue, then dark brown, by Zn. K₄FeCy₆Aq gives a red pp, and K₄FeCy₆Aq a bright-yellow pp, with aqueous solutions of alkalı niobates, gall tincture gives an orangered pp Nb is estimated as Nb,O₅, the process is sufficiently described under *Preparation* (cf. Rammelsberg, P 186, 177, 362, 144, 56, 191)

Niobium, acids of, and their salts Niobia exide, Nb₂O₅, reacts with alkali oxides to form salts, these mobates may be regarded as derived

from various hydrates of Nb₂O₅ Hydrated niobic oxide, Nb.O. xH2O, is obtained by fusing Nb₂O₅ with KHSO₄, washing with water, dissolv ing in HClAq, and ppg by NH,Aq, the pp thus obtained by Santesson (Bl [2] 24, 52) contained c 84 p c water, which corresponds with the composition $3Nb_2O_5 4H_2O$ (= $Nb_4O_{11}(OH)_8$) The hydrate $Nb_2O_5 7H_2O$ is obtained, according to Santesson (lc), by reacting on NaNbO₃ with H₂SO₄Aq and drying at 100° (v Hydrates of mobic oxide, p 509) Niobates have not been obtained by neutralising hydrates of Nb₂O₅, but either by fusing Nb₂O₅ with basic oxides or carbonates, or by double decomposition from solutions of alkali niobates

NIOBATES The niobates belong to the form $xNb_2O_3yMO_3$, where $M=K_2$, Ca, Mg, Mn, &c Niobates are known corresponding with the meta- and pyrophosphates, and, besides these, salts have been isolated in which the ratio of the basic to acidic oxide varies from 1 2 to 4 1 The mobates are prepared by fusing Nb2O, with basic oxides, carbonates, and a few other salts, some mobates are obtained by ppg solutions of alkalı mobates by solutions of metallic salts The alkalı mobates are soluble in water, the Solutions of the alkali others are insoluble niobates are decomposed by H₂SO₄Aq with ppn of Nb₂O₃ xH₂O, CO₂ ppts acid salts Solutions of niobates in HClAq are reduced by Zn to Nb₃O₃ (blue), and then to Nb₂O₄ (brown black) (v Niobium oxides, p 508) Fluoriobates and fluoxymiobates are also known (v next page)

Potassium niobates (1) Metaniobate, Small rectangular tablets, sol water, KNbO, obtained by dissolving Nb₂O₃ in molten CaF, fusing the product with K₂CO₃, in ratio K₂CO₃, Nb₂O₃, and repeatedly treating the mass (after cooling) with boiling dilute H2SO, Aq (Joly, Fremy's Encyclop Chimique) (2) Pyroniobate, K,Nb,O, 11H,O Insol water, obtained by K₁Nb₀O, 11H₁O Insol water, obtained by melting Nb₂O₃ with a large excess of K₂CO₃, and washing with water (Santesson, Bl [2] 24, 52) (3) 3Nb₂O₃ 4K₂O 16H₂O₃ and (4) 7Nb₂O₅ 8K₂O 32H₂O The former salt is obtained by fusing Nb2O5 with 2 to 3 times its weight of K₂CO₃, dissolving in water, and evaporating in vacuo, large monoclinic crystals, efflorescent in air, loses 12H₂O at 100°, and is dehydrated at red heat The second salt is obtained in quad ratic octahedra by slowly evaporating a solution of the first salt (Marignac, A Ch [4] 8, 5, 13, (5) 2Nb₂O₅ 3K₂O 13H₂O, rhombic pyramids, by adding KOHAq to solution of salt (3) or (4), and evaporating slowly (Marignac, lc). (6) $2Nb_2O_3$ $2K_2O$ $11H_2O$, the crystalline residue obtained by fusing Nb_2O_3 and K_2CO_3 , in the ratio Nb₂O₅ K₂CO₃, and treating with water, has this composition (Santesson, Bl [2] 24, 52) (7) 4Nb.O, $3K_2O$, obtained by strongly heating Nb_2O , with twice its weight of KHSO, for some hours, and washing with water (Joly, Fremy's Encyclop Chimique) (8) 3Nb₂O₅ K₂O 5H₂O₅ prepared by boiling KNbOF, 2KFAq with KHCO₃, washing the powder which separates, and drying at 100° (Marignac, lc)

Sodium niobates (1) Metaniobate, 2NaNbO, 5H₂O Rhombic prisms, obtained by fusing Nb₂O₅ with 3 pts Na₂CO₂, allowing to stand in contact with cold water (which dissolves Na.CO.), dissolving in hot water, and crystallising NIOBIUM 507

(Joly, Fremy's Encyclop Chimique) Santesson (Bl [2] 24, 52) obtained this salt by boiling $\mathrm{Nb}_2\mathrm{O}_3\,\mathrm{xH}_2\mathrm{O}$ with NaOHAq, the salt remained insoluble in NaOHAq, slightly soluble in cold water (2) 4Nb₂O₃ Na₂O H₂O, a salt, probably with this composition, was obtained by Santesson (lc) as a gelatinous pp by passing CO_2 into solution of NaNbO₂ (3) 3Nb₂O₃ 2Na₂O 9H₂O. An insoluble amorphous salt, obtained by fusing Nb₂O₃ with NaOH and treating with water (Santesson, lc)

Niobates of Ca, Mg, and Mn—viz Ca₂Nb₂O₂, Ca(NbO₃)₂, Mg,Nb₂O₂ 2MgO, Mg,Nb₂O₂, MgO, Mg₂Nb₂O₃, Min(NbO₃)₂—have been obtained by Joly (lc) by fusing CaCl₂, MgCl₃, and MnCl₃, with NbO₃ Joly also obtained a niobate of Fe, and a niobate of Fe and Mn H Rose (P 90, 456) obtained niobates of Cu, Hg, and Ag by adding salts of these metals to solutions of

NaNbO,

FLUONIOBATES These salts, which may also be regarded as compounds of NbF₅ with metallic fluorides, and sometimes also with HF, are obtained by dissolving Nb,O₅ xH,O in large excess of HFAq, adding metallic carbonates, and evaporating, the fluoriobates are also formed by dissolving fluoryniobates (v infra) in HFAq and evaporating (Marignac, A Ch [4] 13, 5, San tesson, Bl [2] 24, 52) The following are the principal fluoriobates —

(NH₄)₂NbF₂, 2NbOF₃ NH₄F₄,
Co₅Nb₅F₂, 5HF 28H₂O
(= 3NbF₃ 5CoF₂, 5HF 28H₂O),
Cu₄Nb₅F₃ HF 18H₂O),
Cu₅Nb₅F₄ CuF₂ HF 18H₂O),
Fe₂NbF₃ 19H₄O (= 2NbF₃ 3FeF₂ 19H₂O);
Mn₃Nb₅F₂, 5HF 13H₂O,
N1₃Nb₅F₂, 5HF 13H₂O),
N1₃Nb₅F₂, 5HF 28H₂O),
KNbF₃ 5NiF₃ 5HF 28H₂O),
KNbF₄ 5NiF₃ 5HF 28H₂O),
KNbF₄ 5NiF₄ 5HF 28H₂O),

K₂NbF₁(NbF₃ 2KF)
FLUOXYNIOBATES These salts are obtained by dissolving Nb₂O₃ with alkali fluorides in HFAq, and evaporating They may be regarded as derived from the hypothetical acids II,NbOF₃, H₂NbOF₆, and H₂NbOF₇, they may also be looked on as compounds of NbOF₃ with alkali fluorides The fluoxyniobiates have been examined chiefly by Marignac (A Ch [4] 8, 5, 13, 5)

Ammonum fluoxynvobates 1
(NH₄)₂NbOF₅ (= NbOF₂ 2NH₄F) Obtained by dissolving Nb₂O₅ and NH₄F in HFAq, and eva porating, easily soluble rhombic prisms, iso morphous with WO₂F₂ 2NH₄F - 2 (NH₄)₃NbOF₆ (= NbOF₃ 3NH₄F) Obtained similarly to the foregoing salt, forms octahedral crystals, iso morphous with ZrF₆ 3NH₄F (Baker, C J 35, 762) --3 (NH₄)₄NbOF₆ (= NbOF₃ 4NH₄F) Obtained by dissolving Nb₂O₃ H₂O in coinc NH₄FAq, cubic and octahedral crystals of the regular system (Joly, P 108, 467) -- 4 (NH₄)₄Nb₂O₄F₄ H₄O (= 3NbOF₅ 5NH₄F H₄O) Obtained by adding less than an equivalent of NH₄F to Nb₂O₃ in HFAq, and evaporating

Potassium fluoxyniobates — 1
KNbOF, H.O (-NbOF, 2KF H.O) Obtained by
evaporating a solution of Nb.O. in HFAq after
addition of KF By crystallising from water,
the salt separates in such fine tablets that the
liquid appears to gelatinise, monoclimic tables
are obtained by crystallising from water contain-

ing a little HF Loses H₂O at 100°, melts at red heat, sol in 12-13 pts water at 17°-21°, easily soluble in hot water —2 K₂NbOF₄ (=NbOF₃3KF) Obtained by adding excess of KF to solution of the foregoing salt Cubical crystals belonging to the regular system (Baker, C J 35, 761)—3 K₂Nb₂O₂F₁₄H₂O (=3NbOF₃6KF H₂O) Obtained by adding less than an equivalent of KF to Nb₂O₃ in HFAq, evaporating alittle, separating from K₂NbOF₃ HO, which separates, and evaporating the mother liquor —4 K₂NbOF₃ HF(=NbOF₃3KF HF) Obtained by dissolving Nb₂O₃ in considerable excess of HFAq, and adding excess of KF, isomorphous with SnF₄3KF HF

Fluoryniobates of Cu and Zn have also been obtained, CuNbOF, 4H₂O, and ZnNbOF, 6H₂O

Niobium, alloys of An alloy of Nb with Al, approximately of the composition Nb₂Al₃, was obtained by Marignac (Ar Sc 31, 89) by heating NbF₂SkF with Al in a carbon crucible, and treating with cold HClAq A grey, crystalline, metal like powder, SG 445 to 452 Soluble in hot HClAq with evolution of H Insoluble in HNO₃Aq or dilute HSO₄Aq, boiling conc. H₂SO₄ forms SO₂ and S, soluble in HFAq

H₂SO₄ forms SO₂ and S, soluble in HFAq

Niohum, bromide of NiBr₅ Formula probably molecular, because of similarity with

NbCl₅, which has been gasified A purple red

solid, obtained by passing CO₂ laden with Br

vapour over a heated mixture of Nb₂O₅ and C

(H Rose, P 104, 442)

Niobium, carbide of By heating to c 1500° a mixture of 4 pts Nb₂O₃, 1 pt sugar carbon, and 1 pt Na₂CO₃, Joly obtained large violet needles of the composition NbC (Bl [2] 25, 206)

of the composition NbC (Bl [2] 25, 206)
Niobium, carbonitride of By heating Nb₂O₄
with a mixture of Na₂CO₃ and C to c 1200°,
Deville (C R 66, 180) obtained a crystalline
mass, which evolved NH₃ when heated with
molten KOH, according to Joly (Bl [2] 25, 206),
this substance is either a carbonitride of Nb, or
a mixture of carbide. NbC, with nitride NbN

a mixture of carbide, NbC, with nitride NbN Niobium, chlorides of Two chlorides of Nb

are known, NbCl, and NbCl,

NIOBUM PENTACHLORIDE NbCl, Mol w 270 85 V D 138 9 (Deville a Troost, C R 60, 1221) Melts at 194° and boils at 240° (D a. T, lc)

Preparation — Perfectly dry Nb₂O₃ is mixed with a large excess of dry sugar or starch, the mixture is completely charred by heating in a closed crucible, and a small quantity is then placed in a rather wide tube of hard glass, narrowed here and there, connected with a CO₂ and a Cl apparatus, the tube is gently heated for some time while a stream of perfectly dry CO₂ is passed through it, and is then allowed to cool in the CO₂, when cold, perfectly dry Cl is passed through the tube, when every trace of CO₂ is expelled, the tube is gradually heated to bright redness in the stream of Cl, NbCl₃, mixed with a little NbOCl₃, collects in the wider parts of the tube The NbCl₄ is separated from the less volatile NbOCl₄ by distillation in dry Cl

As NbCl₃ is very voluminous the operation must be conducted in wide tubes and with small quantities of the mixed Nb₂O₃ and C (H. Rose)

Properties and Reactions—Yellow needles, melts at 194°, beginning to sublime at 125°, boila at 240° (Deville a Troost C R 60, 1221). Vapour

508 NIOBIUM.

is yellow Soluble in alcohol Fumes in air. giving off HCl Decomposed by water to HCl and $Nb_2O_5 xH_2O$ Soluble in cold conc HClAq; Zn produces a blue colour in this solution, on dilution and heating, Nb₂O₂ xH₂O separates. Soluble in conc H₂SO₄ with evolution of HCl. Vapour of NbCl, is reduced to Nb by heating with H (Blomstrand, Roscoe, C N 37, 25)
NbOCl, is produced by heating with Nb₂O₂
Nb₂O₂S₂ is formed by heating in CS₂ vapour (Delafontaine, Ar Sc 27, 167)

NIOBIUM TRICHLORIDE NbCl. When vapour of NbCl, is slowly passed through a red-hot tube, a dark grey metal like crust forms on the sides of the tube, this crust is NbCl, (Roscoe, C N 87, 25) Not volatile, non-deliquescent, unchanged by H2O or NH2Aq, by HNO3Aq gives HCl and Nb₂O₃ xH₃O Heated in air, gives off white fumes When heated in CO₂, produces CO

and NbOCl.
Niobium, fluoride of No fluoride of Nb has been isolated with certainty Nb2O5 xH2O dissolves easily in HFAq, on evaporation a noncrystallisable mass is obtained, which evolves white fumes when heated and leaves Nb₂O₅ Solution of Nb,O,xH,O in HFAq yields fluoniobates when mixed with metallic carbonates and evaporated, these fluoniobates may be regarded as compounds of NbF, with metallic fluorides (v

Fluonrobates, p 507)

Nichium, haloid compounds of. The only haloid compound of Nb which has been gasified is NbCl, , the trichloride is also known, and the formula NbCl, is probably molecular No fluoride or modide has been isolated, but several compounds are known, which may be regarded as formed by the union of NbF, with more positive fluorides (v Fluoriobates, p 507) NbCl, reduces CO₂ to CO at a high temperature Oxyhaloid compounds are known, of the form NbOX, where X = Br, Cl, or F

Niobium, hydride of, ?NbH Marignac (Ar Sc 1868) obtained a heavy grey powder, having approximately the composition NbH, mixed with a little Nb₂O₈, by heating K₂NbF₇, mixed with a little KHF2, and covered with NaCl, with excess The reaction was of Na in an iron crucible energetic, the fused mass was broken up, treated with water, then with water containing a little HF, then washed with water, and finally filtered and dried The powder obtained by Marignac had S G 6 to 66, it dissolved in conc HFAq with rapid evolution of H, it was insoluble in HClAq, HNO, Aq, and dilute H2SO, Aq, sol warm conc H.SO, also in molten KHSO, heated in air or O to above 100° it burned to Nb₂O₅ and H₂O, it was unchanged when heated in H Krüss a Nilson (B 20, 1691) repeated Marignac's experiments, using a quantity of Na equivalent to the K,NbF, they obtained a mixture of c 77 pc NbH, c 215 pc Nb₂O₅, and c 1 pc Fe₂O₅ K a N give S.H of NbH as 097 at 0° to 100°, 092 at 0° to 210 5°, 087 at 0° to 301 5°, and 088 at 0° to 449°.

Niobium, nitride of, ? NbN NbCl, absorbs NH₂, on heating, NH₄Cl is evolved, and a black mass remains which contains N Heated with KOHAq, NH, 18 evolved, 1t 18 not attacked by HNO, Aq; soluble in HFAq; heated in air, it oxidises with incandescence. The composition of this body is approximately NbN (H Rose;

Deville, C R 66, 180, Joly, Bl [2] 25, 206). By reducing Nb₂O₅ with a mixture of sods and O, Deville obtained a crystalline mass, probably a mixture of nitride and carbide of Nb

Niobium, nitro-carbide of, v Niobium, car-

bonitride of, p 507

Niebium, oxides of Three oxides of Nb have been isolated, NbO, NbO₂, and Nb₂O₅, a fourth, Nb₂O₅, probably exists Nb₂O₅ is formed by heating Nb in air or O, also by decomposing NbOCl, by water, and in other ways, NbO₂ is produced by the partial reduction of Nb₂O₃ in H, NbO is obtained by the incomplete reduction of NbOF, or NbOCl, by Na or Mg, when Nb2O, in HClAq is reduced by Zn the solution becomes brown, and a solid separates, which is probably Nb₃O₅ Moist Nb₂O₅ reacts as an acid forming oxide, niobates are formed by fusing Nb2O5 with basic acids or carbonates (v Niobates, p 506) The mol w of none of the oxides of Nb is known with certainty

NIOBIC OXIDE Nb₂O₄ (Niobic anhydride

Niobium pentoxide)

Occurrence - Niobates occur in a few rare minerals, e g columbite, tantalite, and samarsk-

Preparation -1 NbOCl₃ is agitated with water, the insoluble $Nb_2O_6xH_2O$ is washed till free from HCl, dried at 100°, and heated to in cipient redness The solution after treating NbOCl, with water contains much Nb,O,, the oxide is obtained by adding slight excess of NH, Aq, warming till every trace of NH, is removed, collecting the pp, washing till free from HCl, and drying -2 Dilute H₂SO₄Aq is added to a boiling solution of NaNbO₃, the ppd Nb₂O₅ xH O is thoroughly washed and heated — 8 Impure Nb₂O₅ is fused with KHSO₄, the fused mass is treated with water, and the pp is washed and heated.—4 Nb₂O₅ is obtained in crystals by dissolving in molten borax, heating in a porce lam oven, washing, and drying (Nordenskjold, P 114, 612, Ebelmen, A Ch [3] 33, 34, Knop, Z K 12, 610, also by strongly heating Nb₂O₄ (from NbOCl₃) in a slow current of HCl (Deville, C R 66, 180) For preparation of Nb₂O₅ from columbite v Niobium, Preparation, p 505

Properties -A white powder, becomes yellow when heated, and goes white on cooling Insoluble in water SG 444 to 453 (Marignac, A Ch [4] 8, 5) The crystals of Nb₂O, are flat, right angled tablets, they are optically active (Nordenskjold, P 114, 612, of Ebelmen, A Ch [3] 33, 84, Knop, A 159, 56) SH 118 at 0° to 210 5°, 124 at 0° to 301 5°, 134 at 0° to 449° SH 118 at 0°

(Krüss a Nilson, B 20, 1691)

Reactions —1. Dissolves in hot conc sul phuric acid, the solution may be diluted with out ppn, but on heating all the Nb2O5 is ppd, the pp contains H₂SO₄ -2 Boiling hydrochloric acid dissolves only traces of Nb_2O_a , the residue is easily soluble in water, and this solution is ppd on boiling with H₂SO,Aq (Wöhler, P 48, 93, Marignac, A Ch [4] 8, 15, 13, 20, H Rose, P 112, 484).—8. Easily dissolved by cold hydro fluoric acid -4. Soluble in caustic potash solution -5. Caustic soda does not dissolve Nb.O. but the product is soluble in water which has been strongly heated is insoluble in H₂SO₄, HClAq, or HFAq, it is dissolved by molten alkalis. - 6. Reduced by hydrogen to NITRATES. 509

NbO₂ at full red heat —7 Moist Nb₂O₅ dissolved in HClAq is reduced by sino with formation of a blue liquid which then becomes brown and de positis brown flooks, probably of Nb₂O₅ (Marignac, A Ch [4]18,5) —8 Strongly heated with hydrogen sulphide, or carbon dissulphide, an oxysulphide is formed, probably Nb₂O₅ (Delsfontaine, Ar Sc. 27, 167) —9 Heated with ammonia, Nb nitride (q.v) is formed—10 Mixed with carbon and heated in chlorine or bromine, NbCl₅ (or NbBr₅) is formed along with some NbCl₅ (or NbOBr₈)—11 Fused with basic oxides or carbonates, niobates (q. v) are produced

Combinations —1 With water to form various hydrates (v iu/ra) —2 Nb₀, appears to combine with some acids, but no definite compounds have yet been isolated, eg the pp obtained by decomposing NbOCl, by water in presence of Na₂HPO₄ contains H₂PO₄, and the pp obtained by adding water to Nb₂O₅ in HSO₄ and boiling contains H₂SO₄ (v Blomstrand, Acta Univ Lund 1864)

HYDRATES OF NIOBIC OXIDE Various hydrates of Nb_O₃ are known By fusing Nb₂O₃ with KHSO, boiling with water, dissolving the pp in HClAq, and ppg by NH₄Aq, Santesson (Bl [2] 24,52) obtained a flocoulent pp containing 8 04 to 8 41 pc H₂O, agreeing with the formula 3Nb₂O₄ 4H₂O. The solid obtained by ppg NaNbO₂Aq by HSO₄Aq and drying at 100° has the composition Nb₂O₄7H O, according to Santesson (lc). The hydrate obtained by decomposing NbOCl₃ by water is amorphous, that formed by the action of moist air on NbOCl₃ is said to be crystalline (H Rose, P 112, 557). The hydrates of Nb₂O₃ react as weak acids (v Nvobates, p 506)

Niobous oxide NbO (Niobium monoxide)
By reducing NbOF, 2KF with Na, H Rose obtained a black powder which he thought to be
Nb (P 104, 312) This substance was recognised
as an oxide by Delafontaine (Ar Sc 27, 167)
Prepared by strongly heating NbOF, 2KF with
Na, under KCl, and washing with cold water
SG 63 to 667 Obtained in crystals by passing
vapour of NbOCl, over heated Mg wire (Deville
a Troost, C R 60, 1221, v also Deville, C R
66, 183) Black, lustrous, regular crystals
Moist NbO is soluble in boiling dilute HClAq,
or in HFAq, H is said to be evolved KOHAq
dissolves NbO, forming K niobate Molten
KHSO4 forms Nb2O3, heated in Cl NbOCl3 is
produced

NIOBIUM DIOXIDE NbO₂ (Nuobium tetroxide [Nb₂O₃)) A black powder with blue reflection, insol water and acids Formed by heating Nb₂O₃ in a stream of H to full white heat (Dela-

fontaine, Ar Sc 27, 167)

Wöhler (P 48, 93) noticed that Zn reduces a solution of Nb₂O₅ in HClAq, with production of blue and then brown coloured substances Mazignac (A Ch [4] 13, 5) obtained a bluebrown pp by boiling Nb₂O₅ xH O with HClAq, dissolving the residue in water, and reducing by Zn

Niobium, oxybromide of, NbOBr, A voluminous, crystalline, yellowish solid, obtained by passing Br vapour over a heated mixture of Nb₂O₄, with a little charcoal (H. Rose, P 104, 442) Sublimes without melting Heated in CO₂ gives Nb₂O₄ and NbBr₄. Decomposed by water, giving Nb₂O₄.xH₂O and HBrAq

Miobium, exychloride of, NbOCl₂. Mol. w 216 1 Obtained, along with NbCl₃, by heating Nb₂O₃ mixed with charcoal in a stream of Cl₂ also by heating Nb₂O₃ in a stream of CO₂ charged with vapour of NbCl₃ (Deville a Troost, C. R 60, 1221) A white, lustrous mass, sublimes at ϵ 400° without melting V D at 440° to 810° = 114 (D a T, lc) Heated strongly in CO₂, NbCl₃ and Nb₂O₃ are formed, the same products are formed by heating in H (Blomstrand, Acta Univ Lund, 1864) Sol alcohol, decomposed by water to Nb₂O₃ xH₂O and HClAq

Niobium, oxyfluoride of, NbOF, Small crystals, optically active, resemble ZrF₄, obtained by strongly heating Nb₂O₅, mixed with a large excess of CaF₂ in HCl (Joly, C R 81, 1266) NbOF, forms various compounds with metallic fluorides (v Fluoxymobates, p. 507)

metallic fluorides (v. Fluoxynnobates, p. 507)
Niobium, oxysulphide of, Nb₂OS₃. A black
powder, obtained by passing H₂S or CS₂ vapour
over strongly heated Nb₂O₃. The product of
these reactions was supposed by H Rose to be a
sulphide of Nb (P 111, 193, v also Rose a Hermann, J pr 111, 393) Delafontaine (Ar Sc
27, 167) showed the substance to be an oxysulphide, Rammelsberg (J pr. 108, 95) thought
the composition was NbOS or Nb₂O₃.

Nichium, salts of No compounds obtained by replacing the H of acids by Nb have yet been isolated There are indications that Nb₂O₅ combines with some acids (v. Nichico carde, Combinations, No 2, supra)

M M P M

NITRANILIC ACÍD v. DI NITRO DI OXY-QUINONE

NITRANILINE v NITROANILINE

NITRATES Salts of nitric acid, HNO. The greater number of the nitrates are normal salts, many basic nitrates also exist general formula for normal nitrates may be written $M^n nNO_s$, where M^n denotes a metal of n valency. The normal nitrates may also be regarded as composed of a basic and an acidic radicle, on this view, they are classed under the general formulæ M₂O N₂O₅, MO N₂O₅, MO N₂O₅, MO N₂O₅ The simplest way of looking at the composition of the basic nitrates is to regard them as compounds of the acidic radicle N2O5 with more than the normal quantity of base, thus normal lead nitrate is PbO N2O50 and basic lead nitrate is 3PbO N2O, Several basic nitrates may be formulated as salts of the hypothetical orthonitric acid H₂NO₄, which bears the same relation to ordinary, or meta, nitric acid that orthophosphoric bears to metaphos phoric acid, thus basic lead nitrate 3PbO N2Os

may be written Pb_s(NO_s)₂.

Some nitrates occur native, e.g. Ca(NO_s)₂,
Mg(NO_s)₂, KNO₃, NaNO₃, Alkalı nitrates are
found in river, spring, and drainage waters, and
in the juices of some plants. With regard to
the formation of nitrates in the soil v Nitrairication, this vol. Nitrates are prepared by dissolving metals, metallic oxides or carbonates, in
mitric acid, also, in some cases, by double decomposition from the alkali nitrates

Most nitrates are crystalline salts. As no nitrate has been gasified, the formulæ of these salts are not necessarily molecular. The normal nitrates are soluble in water, a few, eg Bi(NO₃), are decomposed by water with production of in soluble basic nitrates. Nitrates are decomposed

510 NITRATES.

by heat, a few give off HNO, but in almost all cases O is evolved, along with oxides of N and H.O., the final residue is generally a metallic oxide corresponding with the nitrate used, AgNO, leaves a residue of Ag Heated with combustible bodies, nitrates cause deflagration or explosion, if the combustible body be an scid forming element, or a compound capable of forming an acid by oxidation, a salt is formed composed of the metal of the nitrate and the scid produced from the combustible body Thus K₂SeO, is formed by deflagrating KNO, with Se, and K2MnO, by deflagrating KNO, with an oxide or salt of Mn Alkalı nitrates are reduced to NH₃ by the action of potash and zinc, or by a pair of metals one of which is distinctly more electro-positive than the other, eg by Cu and Zn, Fe and Zn, Pt and Zn, &c Alkali nitrates are also reduced to NH, by the action of common putrefactive organisms in presence of peptones and air, also by Pt black charged with O, in the presence of dextrose (v Loew, B 23, 675) Nitrates are reduced to nitrites, N2O, NO, and N, by organisms present in the soil (v Warrington, C J 45, 669, 53,742 [references are given here to other memoirs], 59,484, Munro, C J 49,667)

The greater number of the nitrates are insoluble in conc nitric acid A few dissolve in a large quantity of the acid, according to Ditte (A Ch [5] 18, 320) these nitrates combine with HNO₃ to form acid salts, eg KNO₄2HNO₃, NH₄NO₃ HNO₅, KNO₅3HNO₅, RbNO₅5HNO₅ Some other hydrated nitrates dissolve in warm HNO, Aq when dehydrated, on cooling, hydrates are deposited containing less water than those which crystallise from water, to this class of nitrates belong Mg(NO₃)₂, Mn(NO₃)₂, Zn(NO₃)₂, $Al(NO_3)_3$, $Cu(NO_3)_2$ (Ditte, lc)

The methods of detecting and estimating nitrates are numerous, reference must be made

to Manuals of analysis

The normal salt, Aluminium nitrates Al(NO₃)₃ 9H₂O, obtained by dissolving AlO₃H₃ in HNOsAq, and evaporating, crystallises in oblique rhombic prisms Melts at 73°, deli quescent, e sol H₂O and HNO₃Aq (Ordway, A 76, 247, Salm Horstmar, J 1850 301, Thorey, Russ Zeitschr Pharm 10, 321) The salt does not react with HCl gas (Thomas, C J 33, 367) Basic Al nitrates are obtained by digesting

Al(NO₃)₃ with AlO₃H₃ (Ordway, lc)

Ammonium nitrate NH, NO. According to Tissandier (C R 82, 388) this salt is frequently present in rain water. It is obtained by adding a slight excess of NH3Aq to HNO8Aq and evaporating, also by passing the electric discharge through a mixture of H, N, and O, by passing H2S into dilute HNO, Aq, by the interaction of certain metals, eg Sn, with HNO, Aq NH, NO, crystallises in various forms according to the temperature, the crystals formed at 36° are trimetric, those formed at 87° are rhombohedral, and monometric crystals are pro duced at 120° (Lehmann) The specific heats, volume changes, and heats of transformation, of the various modifications have been determined by Bellati a Romanese (Nuovo Cumento, [3] 21, 5, abstract in C J. 54, 106) S G I 707 (Kopp, A 36, 1), 1 709 (Schiff, A 112, 88), for other results v Clarke's Specific Gravity Table, new ed 110 NH₄NO₂ dissolves in H₂O with a large

disappearance of heat S at 18° c 200; saturated solution contains 478 p c NH, NO, and boils at 164° E sol alcohol Deliquesces in boils at 164° E soi alcohol Deliquesces in air, losing NH, and acquiring an acid reaction. Melts at c 152°, decomposition begins at c. 210° and becomes explosive at c 300°, products are H₂O and N₂O, but part of salt volatilises (Berthelot, C R 82, 982), heated very rapidly, NH₂, NO, and NH₄NO₂ are also formed (B) According to B (lc) NH₂NO₃ may be sublimed according to B (lc) NH₂NO₃ may be sublimed. unchanged, by placing the fused salt in a basin covered with filter paper, over which is a paper cylinder filled with coarse fragments of glass, and heating gently not above 190°-200° NH4NO_s condenses considerable quantities of NH, forming a liquid varying in composition according to temperature and pressure (v Divers, Pr 21, 107, Raoult, C R 77, 788) At -10°, and 760 mm, the liquid NH, NO, 2NH, is formed, heated to 28 5° a solid remains, NH, NO, NH, (R, lc), cf Mendelejeff (B 23, 3464), who regards NH, NO, NH, and NH, NO, 2NH, as amides obtained from NO OH ONH, ONH, and NO(OHN4)8, which are the NH4 salts of hypothetical orthonitric acid NO(OH), The liquid compounds of NH, NO, and NH, react with many salts, the reactions generally resembling those of NH_1NO_3 and dry NH_3 combined (for details vDivers, lc) NH4NO3 absorbs dry HCl, forming NH,Cl, after a time a little Cl and NO are evolved (Thomas, C J 33, 367) The Cu Zn couple reduces NH,NO,Aq to NH, and NH,NO, at $\bar{\mathrm{B}}$ P NO is evolved (Gladstone a Tribe, C J33, 150)

Antimony nitrate The compound Sb.O. N.O. is said to be formed by dissolving Sb₄O₆ in cold fuming HNO₃ (Péligot, C R 23, 709)

Barium nitrate Ba(NO_s)₂

Crystallises in tetartohedral forms belonging to the regular system (Scacchi, J 1860 13, Baumhauer, Z K 1, 51, Lewis, P M [5] 3, 453) SG 3 22 to 3 24 (Kremers, J 5, 15, for other determinations vClarke's Specific Gravity Table (new ed), 111) H F [Ba, O, N'O' Aq] = 187,020 (?) (Th 3, 518) Melts at c 593° (Carnelley, C J 33, 278) S 5 at 0°, 7 at 10°, 9 2 at 20°, 11 6 at 30°, 14 2 at 40°, 17 1 at 50°, 20 3 at 60°, 23 6 at 70°, 27 at 80°, 30 6 at 90°, 32 2 at 100°, saturated solution boils at 1019°, SG and petge composition of Ba(NO₂), Ag are as follows (Mulder) -

S G	Po. Ba(NO _s) _s S G		Pc Ba(NO,)	
1 009 1 017 1 025 1 034 1 042	1 2 8 4 5	1 05 1 06 1 069 1 078 1 087	6 7 8 9	

Ba(NO₃)₂ is only slightly soluble in water containing HCl or HNOs, insol alcohol

Ba(NO₂)₂ is prepared by adding to BaCO₂, or orude BaS, enough HNO, Aq to decompose almost the whole of the salt, filtering, and crystallising also by mixing equivalent weights of BaCl2 and NaNO, in solution, and recrystallising the Ba(NO₂)₂ which separates (Bolley, *UC* 1860 330, Kuhlmann, *DP J.* 150, 57, 108, 415) Ba(NO₂)₂ melts at a moderate temperature, at red heat it evolves O, N, and NO, and leaves BaO, according to Rammelsberg (B 2, 147, 7, 542) the residue NITRATES

contains more O than BaO, and has the compo sition Ba₃O₄ Ba(NO₂)₂ is not acted on by HCl gas (Thomas, C = J 83, 867)

The composition of Beryllium nitrates these salts is doubtful They are very soluble in water and difficult to crystallise By double decomposition from BeSO, Aq, and evaporating, Ordway (J pr 76, 22) obtained deliquescent crystals approximating to the composition Be(NO₂)₂ 8H₂O By heating at 100° the crystals lost half of their nitric acid, and a basic salt re mained, soluble in water Other soluble basic salts seem to be formed by adding a little NH, Aq to a solution of the normal salt, and by digesting the normal salt with BeO xH,O

Bismuth nitrates The normal salt has the composition Bi(NO₃)₃ 10H₂O according to Glad stone (J pr 44, 179) and Heintz (J pr 45, 102), according to the more recent work of Yvon (C R 84, 1164) the crystallised salt has the composition 2B1(NO₂), 11H₂O The normal salt is formed by dissolving Bi, Bi₂O₃, or Bi₂(CO₃)₃ in HNO, Aq, filtering through asbestos or powdered glass, and evaporating to the crystallisationpoint Forms large deliquescent crystals, S G 2 823 at 13° (Clarke's Table of Specific Gravities (new ed), 112) Crystals are very caustic, they melt easily in the water of crystallisation, de composition begins at c 75°-80° with production of basic salts (v infra) Decomposed by HCl gas, giving BiCl, and also much Cl, along with NO, H2O, and possibly other oxides of N and Cl (Thomas, C J 33, 367) Various basic salts have been described According to Graham (A 29, 16) $2(B_{1}O NO_{2}) H_{2}O$ is formed by heating the normal salt to 80° , and is not decomposed below 260° (cf Ruge, J 1862 163) Yvon (C R 84, 1164) assigns the composition 4(BiO NO₃) 3H₂O to the salt obtained by heating the normal salt to 120°, and also to the product of the action of water on the normal salt Many basic salts, xB1 O, yN2O, zH2O, seem to be produced by decomposing Bi 3NOs, or a solution of Bi in HNO₃Aq, by water, the composition of the most stable of these subnitrates is BiO NO, H2O, in other cases x, y, and z have such values as 5, 4, and 9, or 5, 3, and 8, or 6, 5, and 9 The composition of these basic salts varies with the temperature of the water used, the amount of wash ing given to the pp, and the length of time the pp is allowed to remain in contact with the acid liquid above it. The compositions of these salts, and the preparation of a salt of constant compo sition for medicinal use, have been examined 68, 1, 129), Ruge (J 1862 163), and Yvon (C R 84, 1164)

Cadmium nitrate Cd(NO₃)₂ 4H₂O prismatic, deliquescent, needles, by dissolving Prismand, definition of the control $[Cd, O, N^2O^3Aq] = 86,000 (Th 8, 518)$ Melts at 59.5°, and boils at c 132° (Ordway, Am S [2] 27, 14) Reacts with HCl gas to produce CdCl. evolving Cl and NO (Thomas, C J 83, 367) Wells (Am 9, 304) describes a basic salt, to this salt he has assigned the composition

2CdO N₂O₃ 3H₂O , obtained by digesting hot Cd(NO₃)₂Aq with CdO, and allowing to cool

511

Cosium nitrate CsNO, Obtained by dissolving Cs.CO, in HNO,Aq, and evaporating, the habitus of the crystals depends on the rate Melts below red heat, when of evaporation strongly heated evolves O, and forms CsNO. S 10 58 at 3 2°, very slightly sol in alcohol (Bunsen, P 119, 1)

Calcium nitrate Ca(NO₂), 4H₂O Occurs in soils when conditions are favourable to produc tion of HNO, and Ca salts are also present This salt is prepared in some countries by the slow decomposition of animal and vegetable matter SG 179 when liquid, and 19 when solid, at 155° (Ordway, J 12, 115) SG of $Ca(NO_2)_2 = 2.5$ at 17.9° (Favre a Valson, C R $HF [Ca,O^2,N^2O^4,4H^2O] = 218,440$, 77, 579) $[Ca,O,N^2O^3Aq] = 177,160$ Prepared by dissolving CaO or CaCO, in HNO, Aq, and evaporating, if the evaporation is continued to dryness the anhydrous salt is obtained The hydrated salt crystallises with difficulty in deliquescent, sixsided prisms, melts at 44°, boils at 132°, remaining clear till c one third of the water has gone, when the anhydrous salt is deposited (Ord way, Am S [2] 27, 14) The dry salt $Ca(NO_3)_2$ melts at 561° (Carnelley, C J 33, 278) De composed at high temperature, giving off O and NO, the partially decomposed salt is phospho rescent (Baldwin's phosphorus), not acted on by HCl gas (Thomas, C \hat{J} 33, 367)

Cerium nitrates Cerous nitrate. Ce(NO₃)₃ 6H₂O, is obtained as a pale rosecoloured, deliquescent, crystalline mass, by dissolving Ce2O3, or CeO, in presence of reducing substances, in HNO, Aq, evaporating, and drying over H_2SO_4 (Lange, J pr 82, 129) Gives off $3H_2O$ at 150°, and decomposes at 200° Forms several double salts with nitrates MNO, and M(NO,), eg Ce(NO,), 2KNO, 2HO, 2Ce(NO,), 3Mg(NO,), 24H₂O These double nitrates have been examined by Lange (lc) and Holzmann (J pr 84, 76), and more recently by Zschiesche (J p) 107, 65) They are obtained by crystallising a mixed solution of Ce(NO_s), and the other nitrate, and also by dissolving CeO, in HNO, adding the other nitrate and a little alcohol, and evaporating Should the metal of the nitrate which is added be capable of forming a higher oxide than that corresponding to the nitrate used, a little of this oxide is sometimes formed at the expense of the O of the CeO2, and the reduction from Ce(NO₃), to Ce(NO₃), proceeds without addition of alcohol, thus, addition of Mn(NO₃)₂ to CeO₂ dissolved in HNO₃Aq produces 2Ce(NO₃)₃ 3Mn(NO₃)₂·24H₂O, with simultaneous formation of a little MnO2 The double cerous nitrates are also formed by dissolving the various metals in an acid solution of CeO, in HNO₃Aq, reduction is effected to Ce(NO₃)₃.

Ceric intrate, Ce(NO₃)₄. Said to be obtained as a reddish yellow mass by evaporating CeO₂ in HNO, Aq, decomposed by hot water forming a basic salt Combines with KNO, and NH,NO, to form 2Ce(NO₂), 4MNO, 3H₂O (Berzelius, P 1, 29)
Chromium nitrates The normal salt,

Cr(NO₂)₂ 9H₂O, as obtained by dissolving CrO₂H₂ in HNO, Aq, evaporating, and crystallising from warm water; the crystals, which form with dif ficulty, are purple oblique prisms, melting at 512 NITRATES.

87° to a green liquid which boils at 1255° (Ordway, Am S [2] 9, 30, 27, 14) Various (Ordway, Am S [2] 9, 30, 27, 14) Various basic salts are described by Loewel (Ph C 1845) 580), Ordway (Am S. [2] 26, 197), and Stewert (A. 126, 86), they are formed by heating the normal salt, by dissolving CrO₃H₃ in solution of the normal salt, and by boiling HNO, Aq with ex-

cess of CrO,H,.

normal Cobalt nitrates The Co(NO₃)₂ 6H₂O, forms red, prismatic, deliquescent crystals, S G 183 at 14° (Boedeker), melts below 100°, at higher temperatures gives off H₂O and oxides of N, and leaves black Co₂O₄. Produced by dissolving Co, or CoCO₃ in HNO₃Aq, and evaporating Easily sol water Franz (*J pr* [2] 5, 274) gives the following table showing p c Co(NO₃)₂ in aqueous solutions at 17.5° tions at 17 5°

P.c. Co(NO _a),	8 G
5	1 0462
10	1 0906
15	1 1378
20	1 1936
25	1 2538
80	1 319
85	1 3896
40	14662
Saturated at 17 5°	1 5382

Thomsen gives HF [Co, O', N'O', 6H'O] 128,880, [Co, O, N'O'Aq] = 84,540 When HCl gas is passed over $Co(NO_s)_2$, $CoCl_2$, oxides of N, and Cl are formed (Thomas, C J 33, 367) Combines with cerous mitrate to form Co(NO₃)₂.Ce(NO₃)₂ 8H₂O (Lange, J pr 82, 129)

Basic salts are obtained by adding NH.Aq to Co(NO₃)₂Aq under different conditions (v Winkelblech, A 13, 148, 253, Habermann, M

5, 442)

Copper nitrates The normal nitrate, Cu(NO₃)₂ 3H₂O, is obtained by dissolving Cu or CuO in HNO, Aq, and evaporating The solution is at first green owing to production of Cu(NO₂)₂. Blue prismatic crystals, S G 2 174 (Hassenfratz, **A** 28, 8) The salt Cu(NO₃)₂ 6H₂O is deposited below 20° HF [Cu, O², N²O⁴, 6H²O] = 96,950 (Th 8, 518) The hexahydrated salt effloresces in air, losing 3H₂O, it melts at 38°, and decomposes at 65°, forming a basic salt hydrated salt melts at 1145°, and decomposes At red heat, Cu(NO₃)₂ evolves N oxides and leaves CuO, it is deliquescent, easily sol water, but ppd again by conc HNO, Aq Franz gives following table (J pr [2] 5, 274) —

c Cu(NO.).
10
20
30
40
44

Cu(NO_s)_s is rapidly decomposed by HCl, with formation of CuCl₂, Cl, NO, and probably N (Thomas, C J 83, 867)

Basic nitrates of Cu are produced by boiling Cu(NO₂),Aq with KNO₂Aq, or by passing N₂O₄ into H₂O holding CuO₂H₂ in suspension, the product is said to be 4CuO N₂O₅ 3H₂O (Vogel a Reinhauer, J 1859 216) For other basic salts v. Graham, T 1837 47, Casselmann, Fr 4, 24; Tutschew, Z. 6, 109

Didymium nitrate Dt(NO_s)_s 6H₂O. Rose red orystals, by dissolving Di₃O₃ in HNO₃Aq and crystallising, S G 2249, loses 6H₂O at 200° Easily sol water and alcohol, forms double salts with Co(NO₂)₂, Ni(NO₂)₂, and Zn(NO₃)₂ (v Marignac, A Ch [3] 38, 148, Hermann, Rep Chim pur 1861 53, Frerichs a Smith, A 191, 346, Cleve, Bl [2] 43, 361)

Erbium nitrate Er(NO₃)₈ 6H₂O Large crys tals, sol water and alcohol Decomposed by heat forming a basic salt 2Er₂O₃ 3N₂O₅ 9H₂O (Hoglund, $B\tilde{l}$ [2] 18, 193, 279, Cleve, C R 91,

Gallium nitrate Ga(NO₃)₃ Obtained by dis solving Ga in HNO3Aq, evaporating at 100° drying in an exsiccator, and heating in a dry air stream to 40° Decomposes at 110°, and at

200° leaves Ga₂O₈ (de Boisbaudran)

Gold nitrates By dissolving $Au_2O_3xH_2O_3$ in HNO_3Aq , a very unstable salt is obtained, Schottlander gives the formula 5(AuO NO₃) H₂O as approximately correct (A 217, 312) The compound Au(NO₃)₃ HNO₃ 3H₂O, which may be called auronitric acid, is obtained in large crystals by dissolving Au₂O₃ xH₂O in HNO₃Aq with special precautions This compound with special precautions. This compound forms shining, yellow, triclinic octahedra, S G 284, it is readily decomposed by heat to 2Au,O, N₂O, 2H,O (Schottlander, A 217, 312) Several salts are known derived from auro nitric acid, they are obtained by dissolving HNO3 Au(NO3)3 along with various nitrates in HNO, Aq, and evaporating The K salts are KAu(NO3), and HK2Au(NO3), (Schottlander,

Indium nitrate 2In(NO₃), 9H,O needle shaped crystals, by dissolving excess of In in HNO₃Aq, and evaporating in an exsiccator Loses 6H,O at 100° at red heat forms a basic salt, then In₂O₃ (Winkler, J pr 94, 1, 102,

Iron nitrates According to Scheurer Kest ner (C R 47, 927), Fe reacts with HNO, Aq SG 1034 to form Fe(NO_a), and NH₄NO₃, with acid SG 1073 Fe(NO₃), is also formed, with acid SG 1115 only Fe(NO₃), is produced, and with more cone acid basic salts begin to be

Ferrous natrate Fe(NO3)2 6H2O is best pre pared by dissolving FeS in cooled HNO, Aq S G less than 112, the liquid is made as nearly neutral as possible by addition of FeS, decanted, evaporated slowly, and strongly cooled The crystals may be kept unchanged at low tem peratures in the mother liquor S 200 at 0°,

800 at 25° (Ordway, Am S [2] 40, 325)

Ferric nitrate Fe(NO₂), 9H₂O (Ordway, Am S [2] 26, 197, 27, 14) Prepared by dissolving Fe in HNO, Aq S G 1 29 till about 10 pc Fe is taken up by the acid, then adding an equal volume of HNO, Aq S G 143, oblique rhombic prisms are deposited on cooling SG 16835 at 20°, nearly colourless, slightly deliquescent. at 20°, hearly colouriess, singlishy definescent, very soluble in water, very slightly soluble in cold $\mathrm{HNO_2Aq}$, melts $47~2^\circ$, acid begins to be given off at 100° , boils 125° , completely decomposed at red heat (Ordway, lc) Hausmann obtained $\mathrm{Fe(NO_2)}_26\mathrm{H_2O}$ (A 89, 109; v also Widenstein, J pr 84, 248) Scheurer Kestner obtained a dihydrated salt (J 1862. 198).

Numerous basic ferric mirates were obtained Ordway (lc) by dissolving FeO_3H_2 in Fe(NO_s)_sAq, and evaporating (v also Hausmann, A 89, 109, and Scheurer-Kestner, J. 1862 193) Basic salts are also produced by heating Fe(NO₃)₃Aq Basic ferric nitrates are slowly resolved by boiling water to normal salt and Fe₂O₃, the change proceeds most rapidly by heating in a sealed tube

Several ferric aceto nitrates, e g

 $Fe(NO_3)(C_2H_3O_2)_2 3H_2O$, $Fe(NO_3)_2(C_2H_3O) 8H_2O$ have been prepared and described by Scheurer-

Kestner (A Ch [3] 63, 422)

Lanthanum nitrate La(NO₃), 6H₂O Large prismatic, deliquescent, crystals, easily sol water and alcohol May be fused without decomposition at c 40°, but at rather higher tem perature HNO, is removed and a basic salt formed completely decomposed at red heat (Ordway) Two double salts,

 $2La(NO_3)_3 3N_1(NO_3)_2 36H_2O$, and

Frenchs a Smith (A 191, 359) Lead nitrates The normal salt, Pb(NO₃)₂ crystallises in octahedra from a solution of PbO or PbCO, in boiling very dilute HNO, Aq or FOCO, in boiling very dilute BNO₃Aq S of 4472 at 4° (Playfair a Joule, C J 1, 137), 4 41 at 15 5° (Holker, P M [3] 27, 214, v also Schroder, P 106, 226, Ditte, B 15, 1438) H F [Pb, N, O*] = 105,500, [Pb, O*, N*O*] = 109,470, [Pb, O, N*O*Aq] = 68,070 (Th 3, 518) S 39 at 0°, 48 3 at 10°, 60 6 at 25°, 80 at 455 101 at 455 101 at 455 1005 at 455 129 at 100° (Magnetic Research). 45°, 101 at 65°, 120 5 at 85°, 138 9 at 100° (Kre mers, P 92, 497) S in alcohol, S G 9282, 4 96 at 4°, 5 82 at 8°, 8 77 at 22°, 12 8 at 40°, 11 49 at 50° (Gerardin, A Ch [4] 5, 129) Insol conc HNO₃Aq Pb(NO₃), is decomposed at low red heat giving PbO, O, and NO. In HCl gas, PbCl, is formed with evolution of NO and Cl (Thomas, C J 33, 367) Forms a compound with lead phosphate, viz

Pb(NO₃)₂ Pb₃(PO₄). 2H₂O (Gerhardt, A 68, 286) Many basic lead nitrates have been described The salt 2PbO N2O, H2O, which formula may be written PbOH NOs, is obtained by boiling Pb(NO₁), Aq with PbO, filtering hot, and allowing to cool (Berzelius, P 19, 312, Pelouze, J pr 25, 486, Persoz, A Ch [3] 58, 191) S G 5 93 (Ditte, C R 94, 1180) Several other basic salts are known, according to Wakeman a Wells (Am 9, 299) the only recrystallisable basic salt, besides Pb OH NO3, is 10PbO 3N2O5 5H O

Lithium nitrate Lino, By neutralising HNO, Aq with LiOH or Li.CO,, and evaporating Rhombic prisms, SG 2334 (Kremers, P 92, $HF[L_1,N,O^3] = 111,615, [L_1,O,NO'] =$ 520) $[113,620, \frac{[L_1^2, O, N O^3Aq]}{97,005} = 97,005 (Th 3, 518)$

Melts at 264° (Carnelley, C J 33, 275) Easily sol water and alcohol Kremers (P 114, 41)

gives following table --

G Lino, Aq at 19 50	Pc LiNO.
1 0769	14 2
1 1346	26 7
1 193	406
1 255	57 5
1 3154	77 4

Lino, slowly reacts with dry HCl, a small quantity of Cl and NO being evolved (Thomas, $(' \ J \ 33, 370)$

Vol III

The hydrated salt Lino, 5H2O is said to be obtained by crystallising below 10° (Troost, A Ch [8] 51, 134)

Magnesium nitrate MgNO, 6H2O in mother liquor from saltpetre plantations, also in some well-waters of Stockholm, according to Berzelius Prepared by neutralising HNO, Aq by magnesia alba, and evaporating Very deliquescent monoclinic crystals (Marignac, J 1856 336) S G 1464 (Playfair a Joule, C S Mem 2, 401) H F [Mg,O²,N²O³,6H O] = 214,530 [Mg,O,N²O³Aq] = 176,480 (Th 3, 518) Very soluble water and alcohol Oudemans (Fr 7, 410) crystals that J 110 and J 110 crystals that J 110 crystals J 110 c 419) gives the table —

c Mg(NO _a),6H _a O	SG Mg(NO,),Ac
1	1 0034
5	1 0202
10	1 0418
15	1 0639
20	1 0869
25	1 1103
30	1 1347
35	1 1649
40	1 1909
45	1 2176
49	1 2397

According to Graham (T 1837 47), 5H2O are re moved from Mg(NO₃)₂ 6H O at c 330° (M P of lead), and the monohydrated salt can be fused without change, but is decomposed at red heat, leaving MgO Einbrodt (A 65, 115) found that acid began to be evolved before five sixths of the water was removed, hence he regarded the heating Mg(NO₃)₂ H₂O as very doubtful By heating Mg(NO₃)₂ 6H₂O until water ceases to come off, a basic salt 3MgO N₂O₃ is obtained, according to Chodnew (4 71, 241) Reacts with HCl gas to form MgCl, Cl and O and H₂O being evolved (Thomas, C J 33, 370)

Manganese nitrate Mn(NO₂) 6H O Small monoclinic crystals (Hannay, C J 33, 269) Obtained by dissolving MnCO, in HNO, Aq, also by dissolving MnO2 in HNO3Aq in sunlight or presence of deoxidisers, and evaporating SG 18199 when solid at 21°, 18104 when liquid at , 18104 when liquid at

21° (Ordway, J 12, 113) H F [Mn,O,N²O,6H O] = 157,700, $[Mn,O,N O^5Aq] = 117,720 (Th 3, 518)$ Decomposed by heat, giving MnO2, Mn2O3, or Mn3O4, according to the temperature Reacts with HCl gas to form MnCl2, with evolution of Cl and NO (Thomas, C J 33, 370) According to Schultz Sellac (Z 1870 646) the salt $Mn(NO_2)_2$ 3 H_2O crystallises from solution in conc HNOsAq

Mercury nitrates Mercuric 2Hg(NO₃)₂ H₂O, is obtained by dissolving HgO in excess of slightly warmed HNO, Aq, and evapo rating over H,SO,, after some minutes the liquid above the crystals has the composition Hg(NO₄), 2H₂O (Millon, A Ch [3] 18, 361) Ditte (J 1854 366) obtained Hg(NO₅), 8H₂O by cooling to -15° a nearly neutral cone solution of HgO in HNO3Aq

Basic mercuric nitrates are readily formed by heating the normal salt, the chief are 2HgO N₂O₃ 8H₂O (Ditte, I_C), 2HgO N₂O₃ 2H₂O (Marignac, J 1855 415), 3HgO N₂O₃ +H₂O, ob tained by the prolonged action of water on any of the other basic salts

Mercuric nitrate forms several double salts LL

514

With HgI, the compounds Hg(NO₁)₂ HgI₂, Hg(NO₃)₂2HgI₃, and 2Hg(NO₃)₂3HgI₂ are formed (Preuss, A 29, 326, Liebig, A 72, 79) These iodo nitrates are decomposed by water, with separation of HgI₂and solution of Hg(NO₃)₂. With HgS, the compound Hg(NO₃)₂ 2HgS is formed, by digesting freshly ppd HgS with Hg(NO₃)₂Aq, also by passing into Hg(NO₃)₂Aq less H₂S than suffices to decompose it wholly.

Mercurous mirate The nitrates derived from Hg₂O have been examined chiefly by Mitscherlich (P 9, 387), Lefort (A 56, 247), Marignae (A Ch [3] 27, 332), and Gerhardt (A 72, 74) HgNO₂ is formed by the reaction of excess of Hg with HNO₂Aq, but if the action is continued basic salts are produced Basic salts are also obtained by decomposing HgNO₂ by water

The normal salt, HgNO₂ 2H₂O, is obtained in colourless monoclinic crystals by reacting on excess of Hg with cold HNO₂Aq S G c 1 2 To prevent admixture of basic salts it is advisable to allow the acid and Hg to remain in contact until crystals cease to be formed, then to warm gently, filter, and allow to crystallise S G 4 78 (Playfair a Joule, C S Mem 2, 401) The crystals efficiesce somewhat in air, they are dissolved without change in a little water, but dilution produces basic salts By heating HgNO₃ with water HgO and NO₂ are formed HgCl is formed when HCl is passed over HgNO₃, and Cl and NO are evolved (Thomas, C J 33, 370)

Basic mercurous nutrates are formed by warming with Hg the mother liquor from the preparation of the normal salt, and by treating the normal salt with water To the salt obtained by the first of these methods Gerhardt gave the formula 3Hg,0 2N,0, H,0, Marignac gave the formula 4Hg,0 3N,0, H,0, Marignac gave the formula 4Hg,0 3N,0, H,0, Gerhardt), obtained by the action of a little boiling water on HgNO, Marignac formulates this salt as 5Hg,0 3N,0, 2H,0 (2) 2Hg,0 N,0, H,0 (Gerhardt, Marignac), obtained by adding much water to HgNO,2Aq

Mercurous nitrate forms double salts with NH_1NO_3 , $Pb(NO_3)_2$, $Ba(NO_3)_2$, and $Sr(NO_3)_2$. The compositions of these salts are expressed by the formulæ $2HgNO_3$ $4NH_1NO_3$ $5H_2O$ (Rammelsberg, P 109, 397), $2M(NO_3)_2 2Hg_2O$ N_2O_3 , where M=Pb, Ba, or Sr (Städeler, A 87, 129)

Mercuroso-mercuric nitrate, Hg₂O 2HgO N₂O₅
This salt is formed by the gradual oxidation of HgNO₃ in air It is best obtained by boiling 1½ parts HNO₂Aq, S G 1 2, with 1 part Hg till all Hg is dissolved, and maintaining the solution near its B P The salt separates as a yellow powder, after a time a white basic mercurous nitrate begins to form (Wittstock, Gerhardt, A 72, 74, Brooks, P 66, 63) Rubbed with NaCl, HgCl and oxychloride are formed, and on addition of water HgCl₂ goes into solution Treated with HCl gas both HgCl and HgCl₂ are formed with evolution of Cl and NO (Thomas, C J 33, 370) The salt may be regarded as derived from orthonitric acid—NO(OH)₃—by replacing H by Hg¹ and H₂ by Hg¹¹

$$\left[\text{NO(OHg)(O_2Hg)} = \frac{\text{Hg_4O 2HgO.N_4O_3}}{2}\right]$$

Nickel nitrates The normal salt, Ni(NO₂)₂ 6H₂O, is obtained, in emerald-green, deliquescent, monoclinic crystals, by dissolving Ni, NiO, or NiCO₂, in HNO₄Aq, and evaporating Melts at 56 7°, and boils at 136 7°, remaining clear till 3H₂O is gone off (Ordway, Am S [2] 26, 197, 27, 14) SG 2 065 at 14°, 2 037 at 22° (Clarke's Specific Gravity Table [new ed], 112) HF [Ni, O², N²O³, 6H²O] = 124,720, [Ni, O, N²O³Aq] = 83,420 (Th 3, 518) Several double salts of Ni(NO₂)₂ are known — with Ce(NO₂)₂, Di(NO₂)₃, and La(NO₃)₃ (v Cerium Nitrates, Didymum Nitrate, Lanthanum With ammonia forms

N₁(NO₃)₂ 4NH₃ 2H₂O (Laurent, A Ch [3] 36, 354), and N₁(NO₃)₂ 6NH₃ 1₃H₂O

(F Rose, Ammon Kobaltverbind [Heidelberg, 1871], 27) Also combines with nickel chlorule and ammonia to form

 $6(N_1(NO_3)_2 4NH_3 H_2O) (N_1Cl_2 6NH_3) 10H_2O$ (Schwarz, W A B 1850 272)

The basic salt 8NiO N₂O₅5H₂O is ppd as a white powder by adding boiling NH₃Aq to a solution of the normal salt (Habermann, M 5, 440)

Palladium nitrates The normal salt Pd(NO₂)₂ xH₂O forms brown-yellow rhombic prisms, very deliquescent, obtained by dissolving Pd in cold HNO₂Aq, evaporating to a syrup at the ordinary temperature, and allowing to stand in a warm place (Fischer, P 10, 607) By dissolving the normal salt in water, and diluting, the Pd is gradually ppd as a basic salt Basic salts are also obtained by evaporating Pd in HNO₂Aq at c 100° to 120°, and treating the residue with water (Fischer, lc, Kane, B J 24, 236)

Platinum nitrates A brown salt, probably Pt(NO₃)₄, is obtained by dissolving Pt()₂xH₂O in HNO₂Aq, or by decomposing Pt(SO₄), Aq with Ba(NO₄)₂Aq, and evaporating (Berzelius)

Potassium nitrate KNO₃ (Netre Saltpetre) Melts at 339° (Carnelley, C J 33, 277) S G 2 0958 to 2 1078 at 4° (Playfair a Joule, C J 1, 137), 2 059 at 0° (Quinck, P 135, 642), 1 072 at M P (Braun, P 154, 190) H F

[K, O, NO²] = 121,485,
$$\left[\frac{\text{K}^2, \text{O,N O'Aq}}{2}\right] = 96,050$$

(Th 8, 518) Heat of solution = -7967 at 15° -7814 at 34° , -7541 at 53° (Tilden, Pr .08, 401) SH 13° to 98° = 23875 (Regnault, A Ch [8] 1, 129) S 13 3 at 0° , 21 at 10° , 31 2 at 20° , 44 5 at 30° , 63 9 at 40° , 85 9 at 50° , 110 9 at 60° , 139 at 70° , 172 at 80° , 206 at 90° , 247 at 100° (Mulder, J 1866 65, v also Tilden a Shen stone, T 175, 23) Schiff gives the following tables (A 107, 87, 293, for more extended tables v Gerlach, Fr 8, 286) —

Jerrael, 27 0, 200)	
Weight of alcohol in 100 parts	Weight of KNOs in 100 parts solution saturated at 15°
0	20 5
10	13 2
20	8 5
30	56
40	4 3
50	2-8
60	17
60	ā i

NITRATES 515

S.G of KNO.Aq at 21°	Weight of KNO, in 100 parts solution
1 1688	24 98
1 1078	16 62
1 0695	11 08
1 051	8 81
1 0337	5 ŏ4
1 017	2 77

S in glycerin S G 1 225 = 10 (Vogel, N R P 16,557) KNO, is dimorphous, it usually crystallises in trimetric prisms, abc = 5891 701, if a drop of KNOsAq is allowed to crystallise slowly under the microscope, rhombohedral crystals are formed (Frankenheim, P 92, 354) If the rhombohedral crystals are touched by a prismatic crystal while the crystallisation is proceeding, they are changed to prismatic, the prismatic may be changed to rhombohedral by heating nearly to the melting point

Occurrence -In small quantities in all vegetable soils, also in most spring and river waters (Boussingault, C R 44, 108) Nitre is found in the soil of caves, in different parts of the world, wherein animal or vegetable matter undergoes putrefaction, and where alkalis or alkaline earths are present to combine with the nitric acid produced (v Nitrification, p 521) Nitre is also found as an efflorescence on the surface of the soil in parts of India, Arabia, South America, and other warm countries, the percentage of KNO_s in a Bengalese soil was found by Davy to be 83 KNO, occurs in the juices of certain plants, notably in the leaves of the castor oil

Formation -1 By the oxidation of nitrogenous matter in presence of air, moisture, and potash (cf Nitrification, p 521) —2 By the action of K₂CO₃ or KOH on Ca(NO₃)₂, or NaNO₃ 3 By the oxidation of NH, in presence of moisture, air, and ferric oxide, and combination of the HNO, formed with KOH (Pesci, G 1875

In the artificial preparation of nitre by oxi dation of nitrogenous matter in soils, the first step is to prepare a soil rich in N containing materials, this is done by mixing porous soil, preferably that left from the lixiviation of a for mer nitre bed, with farm yard manure, animal and vegetable refuse, and wood ashes or cal careous matter, and watering this with urine This soil is then formed into a mound under a shed, and the process of nitrification is allowed to proceed for perhaps a couple of years, air must be freely admitted, and great care must be taken to keep the soil neither too wet nor too About 5lbs crude nitre are obtained, on an average, from 1,000lbs of such soil (for more details v Dictionary of Applied Chemistry)

Preparation -1 By purifying crude nitre prepared from the washings of saltpetre earth. The liquor from the saltpetre earth contains Ca(NO₁)₂, Mg(NO₂)₂, with smaller quantities of KNO, and NaNO, and also alkaline chlorides, K.CO, (wood ashes) is added, the liquid is fil-tered and evaporated, the crude KNO, is then treated with enough boiling water to dissolve all KNO, but not all the NaCl present—S of KNO, at 100° = 247, S of NaCl at 100° = 89—the liquid is boiled for a considerable time, when NaCl separates with CaCO, and MgCO₃, the liquid is then run off, and while crystallising it salt soluble in water (Nilson, B. 13, 1444)

is constantly stirred to insure termation of small crystals containing little mother liquor, the crystals are recrystallised, washed with saturated KNO, Aq (to dissolve the last traces of alkaline chlorides), and again crystallised.—2 From Chili saltpetre (NaNO,), by adding this salt to hot cone K₂CO₃Aq, when Na,CO₃ separates and KNO, remains in solution The mother-liquor 18 evaporated as long as Na₂CO₃ continues to separate, then run off and allowed to crystallise. with constant stirring - 3 By neutralising pure HNO, Aq with pure KOHAq or K, CO, Aq. evaporating, and crystallising

Properties —A white, crystalline salt, dimorphous, SG c 21, easily sol water, solution tastes cool and bitter, melts below red heat to a colourless liquid which solidifies on cooling to a white fibrous mass, known as mineral crystal or salprunellæ At red heat evolves O, and N as temperature increases Deflagrates when heated with combustible bodies (for physical

properties v beginning of article)

Reactions -1 Decomposed by heat, at c 300°-400° O is evolved, and KNO₂ formed, as temperature increases N is evolved, and finally a mixture of K₂O and K₂O₄ remains —2 Evolves O when heated in presence of combustible sub stances such as P, S, Zn, C, &c Hence the use of KNO, in gunpowder, and as an oxidiser when molten -3 Heated with copper foil, nearly pure K,O is formed, a similar change occurs when KNO, is heated with won -4 Most elements are oxidised by heating with KNO, , if the oxide produced is acidic, a K salt of the corre sponding acid is produced -5 Organic compounds are generally burnt (to CO2 and H2O) by heating with KNO₃ -- 6 Reduced by the copperzinc couple, in presence of water, at first to KNO2 and then to NH3, a similar reduction takes place by hydrogen occluded by Pd, Pt, or Cu (Gladstone a Tribe, C J 33, 139, 306) -7 Reacts with hydrogen chloride gas to form KCl, evolving Cl and Noxides (Thomas, O J 88. 367) For methods by which nitre may be valued approximately, or completely analysed, reference must be made to Manuals of Analysis, for an account of the technical applications of nitre reference should be made to DICTIONARY OF APPLIED CHEMISTRY

Rhodium nitrate Rh(NO₃)₃ 2H₂O (?) A gumlike, very deliquescent, mass, obtained by dissolving Rh₂O₃ 3H₂O in HNO₃Aq, and evaporating at 100° till HNO, ceases to be evolved (Claus, J pr 34, 428, Berzelius

Rubidium nitrate RbNO₃ Obtained in long needles, or six sided prisms (according to rate of evaporation) by neutralising HNO, Aq by Rb, CO, and evaporating S 201 at 0°, 485 at 10° When heated evolves O (Kirchoff a Bunsen, P M [4] 22, 55) According to Ditte (C R 89, 641) an acid salt, 2RbNO, 5HNO, is obtained by dissolving RbNO, in HNO, H2O, this salt is decomposed by water or heat

Samarum nitrate Sm(NO₃), 6H₂O yellow prisms, e sol water, S G 2 375 (Cleve, C. N 48, 74, 51, 145)

Scandium nitrate Sc(NO₂)₂(?) Small plates, by evaporating at 100° a solution of Sc₂O₂ in HNO, Aq Decomposed by heat, giving a basic 516 NITRATES.

Silver nitrate AgNO, (Lunar causta) S G 4 238 to 4 528 (Schröder, P 107, 118) S 121 9 at 0°, 227 3 at 19 5°, 500 at 54°, 714 at 85°, 1111 at 110° (Kremers, P 92, 497), S 1622 5 at 125°, 1941 4 at 133° (Thiden a Shenstone, T 175, 23) Saturated solution boils at 125° S in boiling alcohol = 25 Melts at 218° (Carnelley, C J 38, 276) H F [Ag, O, NO·] = 30,745, [Ag, N, O·] = 28,740 (Th 3, 517) Crystallises in trimetric system, a b c = 9433 11 37 S H 16° to 99° = 14352 (Regnault, A Ch [3]1, 129)

Preparation — Pure Ag is dissolved in HNO₃Aq, the solution is evaporated to dryness, the residue is heated gently till all HNO₃ is removed, when it is dissolved in water and crystallised. It solution of Ag in HNO₄Aq proceeds in the cold the liquid becomes blue from solution of N₂O₃, but no gas is evolved, on warming, NO escapes rapidly AgNO₂ may be prepared from Ag which contains Cu by saturating warm fairly cone HNO₂Aq with the metal, adding enough KOHAq to a part of the solution to ppt Ag₂O along with CuO, digesting the pp with the rest of the solution, whereby the remaining CuO is ppd, filtering, and evaporating the filtrate

Properties —White trimetric crystals, solution in water is perfectly neutral to linus paper, has a metallic taste, and is poisonous, melts below red heat, is a powerful caustic, at once destroying flesh when applied to it AgNO₃ is readily reduced by organic matter in light

Reactions—1 Decomposed by heat, leaving Ag—2 With hydrogen chloride gas forms AgCl and HNO3, with evolution of a very little Cl and NO (Thomas, O J 33, 371)—3 With or game matter, eg paper, dust, &c, forms Ag in presence of sunlight—4 AgNO3Aq is slowly and very partially decomposed by hydrogen with ppn of Ag (Russell, C J [2] 12, 3)—5 Ura nous oxide, UO2, ppts Ag, with production of

 $UO_2(NO_2)_2$ (Isambert, CR 80, 1087)

Combinations—1 With ammonia, to form AgNO₂ 2NH₃, by supersaturating cone AgNO₃Aq with NH₃, decomposes above 100°, giving off NH₃ and N (Marignac, P 9, 413, Mitscherlich, A Ch [2] 72, 288, Kane, P 20, 153) Dry AgNO₃ absorbs NH₃ to form AgNO₃ 3NH₃ (H Rose, J 1857 256)—2 With silver bromide, to form AgNO₃ AgBr, by dissolving freshly ppd AgBr in very cone hot AgNO₃Aq (Risse, A 111, 42) AgCl seems to form a similar compound—3 With silver vodide, to form several compound 2AgNO₃Aq is obtained by boil ing very cone AgNO₃Aq with AgI, pouring off, and allowing to cool (Risse, A 171, 23, Riche, A 111, 39, cf Weltzien, A 101, 127, Kremers, J pr 71, 54, Preuss, A 29, 329, Schnauss, Ar Ph [2] 82, 260, Hofmann, A 171, 23, Sturenberg, Ar Ph [2] 143, 12)—4 With ammonium and polassium nitrates to form AgNO₃ MNO₂(M = NH₄ or K) (Ditte, C R 101, 878)

Sodium nitrate NaNO₃ (Cubic saltpetre, Chih saltpetre) S G 2 2606 at 4° (Playfair a Joule, C S Mem 2, 401), 2 246 at 15 5° (Holker, P. M [3] 27, 218), 1 878 at melting point (Braun, P 154, 190) Melts at c 816° (Carnelley, C J 33, 276) H F [Na, N, O] = 111,250, [Na, O, NO] = 118,255,

 $\begin{bmatrix} Na^2, 0, N^2O^5Aq \\ 2 \end{bmatrix} = 91,310 \ (Th \ 3, 518) \qquad \text{Heat}$ of solution -4786 at 16° , -4255 at 54° (Tilden, $Pr \ 38, 401$) $S \ 72 \ 9$ at 0° , $80 \ 8$ at 10° , $87 \ 5$ at 20° , $94 \ 9$ at 80° , 102 at 40° , 112 at 50° , 122 at 60° , 134 at 70° , 148 at 80° , 162 at 90° , 180 at 100° , 200 at 110° , saturated solution freezes at $-17 \ 5^\circ$ (Rudofff, $B \ 2$, 68), contains $216 \ 4$ parts NaNO, in 100 water, and boils at $119 \ 7^\circ$ (Mulder, $J \ 1866 \ 65$, cf Ditte, $C \ R \ 80$, 1164, Maumené, $C \ R \ 58,81$, 81, 107) Schiff $(A \ 110,75)$ gives a table showing $S \ G \$ and $p \ c \$ composition of NaNO, $Aq \ S \$ in alcohol $(614 \ p \ c)$ at $26^\circ = 21 \ 2$ (Pohl, $W \ A \ B \ 6,600$, $v \$ also Wittstein, $Vier \$ tely $Zeit \ Pharm \ 12,109$) 75 parts NaNO, added to 100 parts water at $13 \ 2^\circ$ lower the temperature through $18 \ 5^\circ$ 50 parts NaNO, mixed with 100 parts snow lower the temperature to $-17 \ 5^\circ$

Occurrence —In large quantities in Chili, Peru, and some other parts of South America

Preparation—1 The crude salt is purified by repeated solution and crystallisation, or it is recrystallised once or twice, the first portions of each crop of crystals being rejected, then heated with HNO₃Aq, whereby chlorides are transformed into nitrates and again crystallised 2 By neutralising HNO₃Aq with NaOHAq or Na₂CO₃Aq, and evaporating

Properties —White obtuse rhombohedrons, having much the aspect of cubes, hence the name cubic saltpetre. Absorbs water from moist air. Melts c 316°, and solidifies to white mass on cooling, decomposes at higher temperature similarly to, but more readily than, KNO₂, deflagrates with charcoal, &c, but less quickly than KNO₄.

Reactions — Decomposed by heat at c 350°-380°, evolving 0, and at higher temperature N also — 2 Heated in presence of oxidisable bodies, produces oxides, which, if acidic, form Na salts of corresponding acids — 3 With hydrogen chloride forms NaCl, and evolves NO and Cl (Thomas, C J 33, 367)

Strontium nitrate Sr(NO_s) Prepared by adding to SrCO3 enough HNO3Aq to dissolve nearly all the salt, filtering, and crystallising Separates without water of crystallisation from hot conc solutions, from cold and more dilute solutions crystals of $Sr(NO_3)_4H_2O$ are obtained (Souchay a Lenssen, A 99, 45) The anhydrous salt crystallises in octahedrons, S G 2 98 at 16 8° (Favre a Valson, C R 77, 579)
The hydrate forms triclinic crystals, a b c
= 5895 1 808, S G 2 249 at 15 5° (F a V, lc) HF $[Sr,N,O^3] = 109,910$ (Th 3, 517) S an hydrous salt 20 in cold water, 200 in boiling water Melts at red heat with decomposition, leaving SrO Does not react with HCl gas (Thomas, C J 33, 371) A compound with Sr acetate, VIZ Sr(NO₃)₂ Sr(C₂H₃O)₂ 3H₂O, 13 ob tained by allowing a mixed solution of the salts to evaporate (von Hauer, J pr 74, 432)

Tellurium nitrate The compound STeO₂2N₂O₃ BH₂O is obtained by dissolving Te in excess of hot HNO₂Aq S G greater than 1 15 the salt crystallises in forms which are probably orthorhombic, soluble in HNO₂Aq, easily decomposed by water with separation of TeO₂ (Klein, A, Oh. [6] 5, 59)

Thallium nitrates Thallous nitrate, TINO, is obtained by dissolving Tl in not very conc HNO, Aq, keeping as small an excess of acid as possible, and evaporating Rhombic prisms, S G 5 5 (Lamy a Des Cloizeaux, N 1, 116) S 10 6 at 15°, 43 5 at 58°, 588 at 107° (Crookes, C J 17, 141, Lamy, C R 54, 1255) Melts at 205° without decomposition alcohol and solidifies to a glass S G 58 (Lamy, lc) H F [Tl,N,O³] = 58,150 (Th 8, 517) Strongly heated in a crucible leaves TINO, and Tl.O. (Carstanjen, J pr 102, 65, 129)

Thallic nitrate Tl(NO_s)_s Separates in large deliquescent crystals from solution of TlO OH in HNO₂Aq S G 14, according to Strecker (A 135, 207) the crystals contain 6H O, and according to Willm (A Ch [4] 5, 5) 8H₂O Decomposed

at c 100°

Thorium nitrate Th(NO_s), 12H₂O Large, translucent tables, very hygroscopic, lose 8H₂O over H₂SO₄ Forms a very soluble double

salt with KNOs

Tin nitrates No definite salt has been isolated Stannous oxide dissolves in very dilute cold HNO3Aq, but the solution decomposes on heating with separation of SnO₂ (cf Ditte, A Ch [5] 27, 145) Sn dissolves in cold very dilute HNO, Aq, with production of NH, NO, and probably Sn(NO₃)₂ Freshly ppd SnO₂ dissolves in HNO₂Aq on heating SnO₂ is ppd

Titanium nitrate By evaporating a solution of TiO2 in HNO3Aq over lime, Merz obtained lustrous plates 5T1O2 N2O3 6H2O, soluble in cold

water $(J^{-}pr 99, 157)$

Uranium nitrate By dissolving U or an oxide of U in HNO3Aq, and evaporating, large, yellow, rhombic crystals are deposited having the composition $UO_2(NO_8)_2$ $6H_2O = uranyl nitrate$ SG 2807 (Boedeker) Effloresces somewhat on dry air, melts at 59 5°, and boils at 118° (Ordway, J 1859 114) A trihydrated salt, UO₂(NO₃)₂ 3H₂O, was obtained by Schultz-Sellack (Z [2] 6, 646) by evaporating a strongly acid solution of the ordinary salt over H2SO, and KOH Reacts with HCl to form U oxychloride with evolution of Cl and NO (Thomas, C J 33, 371)

No definite salt has Vanadium nitrates been isolated By dissolving VO or VO, in HNO3Aq, a blue solution is obtained which cannot be evaporated without decomposition (Berzelius) By dissolving V2O, in HNO, Aq, and allowing to evaporate, a reddish residue is ob

tained (Berzelius)

Yttrium nitrate $Y(NO_3)_3 6H_2O$ translucent crystals, by evaporating over H₂SO₄, a solution of Y₂O₅ in HNO₅Aq (Cleve, Bi [2] 21, 344) Heated till NO₂1s evolved, the basic salt 2Y₂O₅ 3N₂O₅ 9H₂O is obtained (v

Bahr a Bunsen, A 137, 1)
Zinc nitrate Zn(NO₃)₂ 6H₂O Zn dissolves in HNO₃Aq with formation of NH₄NO₃ and Zn(NO₃)₂, from very dilute HNO₃Aq, N₂O is Zn(NO₃)₂, from very dilute HNO₃Aq, N₂O is evolved The salt is prepared by evaporating a solution of Zn, ZnO, or ZnCO3, in HNO3Aq Large 4 sided prisms, deliquescent, very soluble water and alcohol, melt at 36 4° and boil at 131° (Ordway, Am S [2] 27, 14), lose 2H₂O in vacuo over H₂SO, (Vogel a Reischauer, N J P 11, 137), lose all H₂O by heating to 105° in stream of dry air (Pierre, A. Ch [3] 16, 247) S. G. 2063 at 13° (Clarke's Table of Specific

Gravities (new ed) 110) H F [Zn,O2,N2O4,6H2O] =142,180, [Zn,O,N²O³Aq] = 102,510 (Th 8,518) The SG of Zn(NO₂)₂Aq and pc of Zn)NO₂)₂ are given by Franz (J pr [2] 5, 274) —

S G	Рc	l) SG	Рe
1 0496	5	1 3268	30
1 0968	10	1 3906	35
1 1476	15	1 4572	40
1 2024	20	1 5258	45
1 264	25	1 5984	50

 ${\rm Zn(NO_4)_2}$ with HCl gas gives ZnCl₂, evolving Ci and NO (Thomas, C J 33, 371) Many basic nitrates of zinc are known, they are obtained by heating the normal salt, by treating HNO, Aq with a large excess of Zn, and by digesting hot $Zn(NO_3)_2$ with ZnO (v Schindler, N J P 11, 137, Vogel a Reischauer, *ibid*, Ordway, *Am S* [2] 27, 14, Grouvelle, *A Ch* [3] 19, 137, Wells, Am 9,304)

Zirconium nitrates The normal salt Zr(NO₂), is said to be obtained by evaporating a solution of ZrO, xH₂O in excess of HNO₂Aq, by heating to 100°, the pyro salt ZrN₂O, is formed, and by boiling a dilute aqueous solution of this, the basic salt 3ZrO, 2N,O, is produced

M M P M

NITRATION v NITRO COMPOUNDS NITRIC ACID HNO, (Spiri (Spirit of nitre Mol w 62 89 (v When dilute, aquafortis) when dilute, aquajorits) Mol w 52.89 (v v) r) [C -4.7°] (Berthelot, Bl [2] 29, 3) (86°) (Mitscherlich, P 18, 152, Millon, J pr 29, 337) S G 1 552 at 12.5° (Mitscherlich, lc), 1552 at 15° (Millon, lc) V D (mixed with dry air) at 40.5° = 34.3 (Playfair a Wanklyn, C J 15, 142, v v; r) r(r) S H of HNO, 10H₂O = 768, HNO, 20H₂O = 240, HNO, 50H₂O = 260, r

 $HNO_3 20H_2O = 849$, $HNO_3 50H_2O = 93$, $HNO_3 100H_2O = 963$, $HNO_3 200H_2O = 982$ (Thomsen, P 142, 337) $HF[H,N,O^3] = 41,510$, $[H,O,NO^2] = 43,515$, $[H,O^2,NO] = 63,085$,

$$\begin{bmatrix} \frac{N^2, O, H^2O}{2} \end{bmatrix} = 7,830,$$

$$\begin{bmatrix} \frac{N O, O^4, H^2O}{2} \end{bmatrix} = 16,200;$$

$$\begin{bmatrix} \frac{2NO, O^3, H^2O}{2} \end{bmatrix} = 28,905,$$

$$\begin{bmatrix} \frac{2NO^2, O, H^2O}{2} \end{bmatrix} = 9,335,$$

 $[N^2,O^5,Aq] = 29,820, [N^2O^3Aq,O^2] = 36,640$ $[2NO^2,O,Aq] = 33,830$, $[N^2O,O^4,Aq] = 47,560$, $[2NO,O^4,Aq] = 72,970$, $[H,N,O^3,Aq] = 49,090$, $[2NO,O^3,Aq] = 72,970$, $[H,N,O^3,Aq]$ $[HNO^3Aq,O] = 18,820$ (Th 2, 199)H V 7250 (Berthelot, C R 90, 1510) For E C of HNO, Aq at different dilutions v Ostwald (J pr [2] 32, 300) Affinity of HNO.Aq approximately the same as HClAq M M 118 (Perkin, C J 55, 680)

Occurrence—In small quantities in rain-

water, varying from c 1 to c 16 pts per million pts of rain, for measurements v Goppelsröder, (Fr 10, 259, 11, 16), Warington (C J 55, 537, references are given to various other results) Ekin $(C \ J \ [2] \ 9, 64)$ found HNO, in the spring water of an uncultivated hill near Bath, not exposed to contact with organic matter Salts of HNO, occur in almost all soils, although not generally in large quantities, and also in the juices of many plants

Nitric acid has been known from early times. Geber mentions it (8th cent), Glauber (17th cent) gave directions for its preparation from nitre by the use of H2SO, Lavoisier showed that this acid contained O, Cavendish proved the presence of N in 1t, and obtained it by passing electric sparks through moist O and N.

Formation -1 By burning H in Oin presence of air (Lavoisier, Kolbe, A 119, 176, Hofmann, B 3, 658) The experiments of L T Wright (C J 35, 42) tend to show, although they do not absolutely prove, that the HNO, is formed by oxidation of NH, not of N-2 By passing electric sparks for some time through a mirture of moist N and O (Böttger, J pr 78, 494, Perrot, C R 49, 204, Buff a Hofmann, A 113, 140) -8 By exploding air with electrolytic gas (H_2+0) (Bunsen) Hempel's experiments (B 23, 1455) show that HNO, is formed when air is burnt with O and electrolytic gas under pressure of several atmos Hempel also proves that considerable quantities of HNO, are formed when C is burnt in compressed air in presence of strongly compressed O -4 By burning air in coal-gas (Ilosva, Bl [3] 2, 734), or coal gas in air (Wright, C J 35, 42) -5 According to Berthelot (C R 108, 543), a very little HNO₃ is formed when ether and P are slowly oxidised by air in presence of water—6 Nitrates are formed by the oxidation of nitrogenous animal or vegetable matter in the soil (v Nitrification) 7 Ozone produces NH₄NO₂ from NH₃, and NH₄NO₂ easily oxidises to NH₄NO₃ (Carius, A. 174, 31, Schönbein, J pr 75, 99, Weith a. Weber, B 7, 1745, Wöhler, A 136, 256) —8 By oxidising NH, in presence of moisture, eg by passing NH, and air over Pt black heated to c. 800°, by distilling (NH₄)₂SO₄ and cone H₂SO₄ with K₂Cr₂O₇, or distilling (NH₄)₂SO₄ with KMnO₄ and dilute H₂SO₄Aq (Tessié du Mothay, W J 1871 280) —9 HNO₄ is a product of the reaction of NO₂ with H₂SO₄, and NaNO₂ is formed by acting on NaOHAq with N₂O₄ (Lunge, B 12, 1058) -10 By heating MnCl₂ or MnSO₄ with NaNO₄ (Kuhlmann, W J 1862 239) -11 By decomposing Ba(NO₃)₂Aq or Pb(NO₃)₂Aq by H₂SO₄Aq, filtering, and concentrating by evaporation—12 By heating NaNO₂ with AlO₂H₄ or SiO₂ (Wagner, D P J 183, 76)

Preparation—1 A mixture of 101 pts thoroughly purified and dry KNO₂, in coarse

powder, and 98 pts pure H2SO, is heated in a capacious glass retort, the neck of which passes some way into a glass receiver which is kept The distillate is again distilled till onethird has passed over, when a quantity of conc H2SO4 equal to the contents of the retort is added (when the retort is cold), the receiver is changed, and distillation is continued, the distillate is again distilled at as low a temperature as possible, to get rid of H2SO4, the distillate thus obtained is gently warmed, and a current of perfectly dry CO2 is passed through it until it is quite colourless, oxides of N are thus removed HNO, may be removed by distilling with a little urea, which decomposes HNO, giving CO, H₂O, and N.—2 Commercial soid is distilled, after addition of a little KNO, to decompose H2SO, until a few drops give no pp, when diluted, with AgNO., the receiver is then changed and distillation continued

Preparation of fuming nitric acid.—The red furning acid consists of a solution of NO, in HNO,, it is a more powerful oxidiser than the

ordinary acid It is prepared by heating e. 202 pts KNO, with 98 pts H,SO, and continuing the distillation as long as liquid comes over, the second stage of the process, which is represented by the equation KHSO₄+KNO₅ = K₂SO₄+HNO₅, occurs only at a temperature so high that part of the HNO, is decomposed with formation of NO. A better method is to arrange the materials so that a portion of the HNO, is reduced to NO, as soon as it is formed; this may be done by mixing 100 pts KNO, with 81 pts starch, placing the mixture in a large retort the beak of which passes inside a glass tube 8 to 4 feet long which tube dips into a glass receiver kept very cold, and adding 100 pts H_2SO_4 The process goes on almost without 8 G 185 About 60 pts red the application of heat fuming acid are obtained from 100 pts KNO. (Brunner, Rép Chim app 8, 188)

Properties —Perfectly pure HNO, has not been isolated, Roscoe obtained an acid with from 99 5 to 99 8 p c HNO_s (A 116, 211) Nitric acid is a colourless, highly corrosive liquid, ac cording to Berthelot it solidifies at $c = 47^{\circ}$, the B P is 86°, but decomposition begins below this temperature, at c 256° the change 2HNO_3 = $2\text{NO}_2 + \text{H}_2\text{O} + \text{O}$ is complete. The following table shows the process of decomposition by heat (Carius, B 4, 828) -

•	8.G of vapour		Pc decom	cc of O from
	Air=1	H=1	position	1g HNO,
86°	2 05	29•6	9 53	8 43
100	2 02	29 1	11 77	10 41
130	1 92	27 6	18 78	16 62
160	1 79	258	28 96	26 22
190	1 59	230	49 34	43 69
220	1 42	20 4	72 07	63 79
250	1 29	186	93 03	82 30
256	1 25	180	100 0	88 47
265	1 24	179		ł
812	1 23	178		

By mixing the vapour from HNO, with dry air, Playfair a Wanklyn (C J 15, 142) found the VD at $40.5^{\circ} = 34.3$, that calculated from HNO. being 31 5 HNO, is slowly and partially decomposed by sunlight, giving NO, O, and HO, so that when exposed to sunlight the soid becomes yellow and contains NO. Solution of HNO. in water, and dilution of the liquid, are accompanied by production of heat, Thomsen (Th 3, 66) gives the following table

	[HNO*,xH*O]	[HNO*.xH*0]
5	2005	1280
1	3285	1
15	4160	1550
25	5276	1389
8	5710	
5	6665	658
10	7818	140
20	7458	-22
40	7436	-15
80	7421	29
100	7489	1
160	7450	45
820	7498	1

If these results are plotted, and a curve drawn, with the horizontal lines showing molecules of H₂O and the vertical lines showing quantities of heat, the curve shows no signs of irregularity; hence. Thomsen concludes that the heat of solution and dilution of HNO, does not indicate the formation of any definite hydrates of HNO, Considering the results which have followed a very close and extended examination of the heat of dilution of H_2SO_4 (v especially Pickering, C J 57, 64), it seems inadvisable to draw conclusions in favour of, or against, the formation of hydrates of HNO, from the limited number of thermal observations made by Thomsen Berthelot (Bl [2] 22, 530) has also measured the heat produced on adding water to HNOs already diluted with known quantities of water, and concludes that a hydrate HNO, 2H2O exists in aqueous solutions of HNO. Perkin has determined the magnetic rotatory power of HNO. and $\text{HNO}_3 x\text{H}_2\text{O}$ (C J 55, 680), his results are $-\text{M M HNO}_3 = 1$ 18, M M $\text{HNO}_3 + 2$ 67H O = 3 656 Now by deducting 2 67 (M M of 2 67 H_2 O) from 3 656, we get 986 as the MM of HNO, in presence of 2 67H,O, but pure HNO, gave MM 118, hence the water has reduced the MM of HNO, by 194 From these results, Perkin concludes that HNO, and H2O combine to form H₃NO,

The electrical conductivity of HNO, Aq for increasing dilution has been measured by Kohlrausch a Grotrian (P M [4] 49, 417) and by Ostwald (Z P C 1, 74) Conductivity increases slightly with dilution, but soon reaches a maximum The behaviour of HNO Aq in this respect is characteristic of that of the strong monobasic acids (cf also Bouty, C R 106, 654) Roscoe (C J 13, 150) has shown that distilling HNO, Aq at 760 mm results in production of an acid containing 68 pc HNO₃, the formula 2HNO₃ 3H₂O requires 70 pc, and HNO₃ 2H₂O requires 68 6 pc, HNO₃, the liquid of constant BP is therefore not a definite hydrate. This liquid boils at 120 5° under 735 mm pressure By distilling at 150 mm pressure, Roscoe obtained an acid containing 67 6 pc HNO₃, at 70 mm (BP 65°-70°) the acid contained 66 7 pc HNOs, at pressure greater than 760 mm rather more than 68 p c. HNO, was present in the acid of constant B P. The percentage of HNO, in the liquid obtained by passing dry air into HNO₃Aq containing from 64 to 68 pc HNO₃, varies with temperature, the higher the temperature the greater the percentage of HNO₃. For every mixture of HNO₃ and H₂O there is a fixed temperature, whereat HNO, and H2O evaporate in the same proportion as they are present in the residual acid, for 662 pc HNO. this temperature is 100°, for 64 5 pc it is 60° (Roscoe, lc, for older observations v Millon, J pr 29, 349, Smith, Ph C 1848 203) When HNO₃ and H₂O are mixed, the maximum contraction takes place for the ratio 2HNO, 3H₂O (Kolb, A Ch [4] 10, 140)

Kolb (A Ch [4] 10, 186) gives the following table, showing weight of HNO, is 100 pts of HNO, aq (p) at 0° and 15°. The numbers marked with an asterisk were directly determined by adding a weighed excess of CaCO, and weigning the residue—

1	8.G.			
	,	at 0°	at 15°	Contraction
	100 00	1 559	1 530	0 0000
	99 84*	1 559*	1 530*	0 0004
	90 42*	1 558*	1 530*	0 0010
1	99 52* 97 89*	1 557* 1 551*	1 529* 1 523*	0 0014 0 0065
1	97 00	1 548	1 520	0 0090
١	96 00	1 544	1 516	0 0120
1	95 27*	1 542*	1 514*	0 0142 0 0182
1	94 00 93 01*	1 537 1 533*	1 509 1 506*	0 0182
	92 00	1 529	1 503	0 0242
	91 00	1 526	1 499	0 0272
	90 00	1 522	1 495	0 0301
	89 56* 88 00	1 521* 1 514	1 494* 1 488	0 0315 0 0354
1	87 45*	1 513*	1 486*	0 0369
1	86 17*	1 507*	1 482	0 0404
	85 00	1 503	1 478 1 474	0 0433
1	84 00 83 00	1 499 1 495	1 474	0 0459 0 0485
	82 00	1 492	1 467	0 0508
	80 96*	1 488*	1 463*	0 0531
	80 00 79 00	1 484 1 481	1 460 1 456	0 0556
	77 66	1 476	1 451	0 0610
	76 00	1 469	1 445	0 0648
	75 00	1 465	1 442	0 0666
	74 01* 73 00	1 462* 1 457	1 438* 1 435	0 0688
1	72 39*	1 455*	1 432*	0 0722
	71 24*	1 450*	1 429*	0 0740
	69 96 69 20*	1 444 1 441	1 423 1 419*	0 0760
í	68 0 0	1 435	1 414	0 0784
-	67 00	1 430	1 410	0 0796
1	66 00	1 425	1 405	0 0806
	65 0 7 64 0 0	1 420* 1 415	1 400* 1 395	0 0818 0 08 30
-	63 59	1 413	1 393	0 0838
	62 00	1 404	1 386	0 0846
	61 21* 60 00	1 400* 1 393	1 381* 1 374	0 0850 0 0854
1	59 59*	1 391*	1 372*	0 0855
	58 88	1 387	1 368	0 0861
1	58 00	1 382	1 363 1 358	0 0864
	57 00 56 10*	1 376 1 371*	1 353*	0 0870
,	55 00	1 365	1 346	0 0874
٠	54 00	1 359	1 341	0 0875
	53 81 53 00	1 358 1 353	1 339 1 335	0 0875 0 0875
.	52 33*	1 349*	1 331*	0 0875
٠	50 99	1 341*	1 323*	0 0872
۱,	49 97 49 00	1 334 1 328	1 317 1 312	0 0867 0 0862
١,	48 00	1 321	1 304	0 0856
1	47 18*	1 315*	1 298*	0 0850
	46 64 45 00	1 312 1 300	1 295 1 284	0 0848 0 0885
	43 53*	1 291*	1 274*	0 0820
3	42 00	1 280	1 264	0 0808
ť	41 00 40 00	1 274	1 257 1 251	0 0796
	39 00	1 267 1 260	1 244	0 0755
	87 95*	1 253*	1 237*	0.0762
	86 00	1 240	1 225	0.0740

	8	Co-t	
	at 0°	at 15°	Contraction
35 00	1 234	1 218	0 0729
83 86*	1 226*	1 211*	0 0718
82 00	1 214	1 198	0 0692
81 00	1 207	1 192	0 0678
80 00	1 200	1 185	0 0664
29 00	1 194	1 179	0 0650
28 00*	1 187*	1 172*	0 0635
27 00	1 180	1 166	0 0616
25 71	1 171*	1 157*	0 0593
23 00	1 153	1 138	0 0520
20 00	1 132	1 120	0 0488
17 47*	1 115	1 105	0 0422
15 00	1 099	1 089	0 0336
13 00	1 085	1 077	0 0316
11 41*	1 075	1 067*	0 0296
7 22*	1 050	1 045*	0 0206
4 00	1 026	1 022	0 0112
2 00	1 013	1 010	0 0055
0 00	1 000	1 999	0 0000

On adding water to the fuming red nitric acid, the liquid becomes green, then blue, and finally colourless when dilute, red vapour of NO₂ is evolved, the more rapidly the higher is the temperature The NO₂ present in the fuming acid is slowly decomposed by the added water, giving HNO₂, which colours the hauid blue (the green colour being the result of the yellow caused by NO2 and the blue caused by HNO, on further dilution NO is evolved, and only HNO, remains

(1) 2NO₂ + H₂O = HNO₃ + HNO₂, (2) 8HNO₂ = HNO₃ + 2NO + H₂O Reactions — 1 Heat decomposes HNO₃ to NO₂, H₂O, and O, the decomposition is complete at c 256° (Carius, B 4, 828) — 2 Light slowly decomposes HNO, in the same way as heat, hence very conc HNO, Aq kept in an open place always contains some NO2 -3 The products of electrolysis of HNO₂Aq vary with the dilution of the acid, with acid 2HNO₃ 3H₂O no H is evolved at first, after a little NO comes off, and then H begins, while the NO slowly ceases, as dilution increases H is evolved and products of reduction -N₂O₂, NO, N, and NH₂—are produced, the more rapid the electrolysis the greater is the quantity of H evolved, very dilute acid evolves H only without the formation of reduced products (Bourgoin, J Ph [4] 13, 266 [abstract in C J [2] 9, 885], Gladstone a Tribe, C J 35, 172) —4 Conc HNO₂Aq is rapidly reduced by hydrogen occluded by Pt or Pd, with oxidation of the H (G a T, lc) -5 HNO₂Aq is also reduced by many metals, the products vary with temperature, concentration of the acid, and the nature of the metal Mg with 68 p c acid plus an equal quan tity, or twice the quantity, of water, produces H along with gaseous reduction products (G a T, C J 85, 178) The gaseous reduction products are generally N2O, NO, and N, these gases are formed by the reaction with HNO, Aq of eg Al, Cd, Co, Cu, In, Fe, Pb, Mg, N1, Ag, Tl, Sn, Zn (Acworth, C J 28, 828, Acworth a Armstrong, C J 82, 54) It appears to be the case that the greater the heat of formation of a metallic oxide the more completely is HNO.Aq reduced by the

metal (cf Thomsen, Th 3, 547) Al, Cd, Fe, Mg, Pb, Sn, Zn, and the alkalı metals produce NH, NO, and NH2OH, but no nitrous acid or nitrites, Bi, Cu, Hg, and Ag produce nitrites but no NH₄NO₃ or NH₂OH (Divers, C J 43, 443, for the combined action of HNO₃Aq and H_2SO_4Aq on Zn v Divers a Shimidzu, C J47, 597) In most cases nitrates of the metals are formed, but sometimes these are decomposed with the final formation of oxides, eg Sb, Sn, and W (v also Veley, Pr 48, 458) Ta, Ti, Au, and most of the Pt metals do not react with HNO₃Aq -6 All the solid non metals are oxidised by nitric acid -7 Oxidisable compounds are oxidised by $\mathrm{HNO_3Aq}$, eg ferrous compounds are changed to ferric, stannous to stannic, arsenious to arsenic, sulphides generally yield sulphates and nitrates -8 Hydrodic acid and sodides yield H₂O, NO, and I -9 Hydrochloric acid gives H2O, NOCl, and Cl (v aqua regia under Chlorhydric Acid, vol 11 p 8, Reactions No 17) -10 Organic compounds are oxidised by HNO₃Aq, straw, hay, cotton, &c, are in flamed by the conc acid (Kraut, B 14, 301) Many organic compounds, especially those of the benzenoid class, form nitro derivatives, H being replaced by NO. -11 With starch, N₂O₃ or a mixture of this with NO, is produced, HNO₃Aq S G 13 to 135 gives almost pure N_2O_3 , if the SG is greater than 135 NO2 is also produced, if S G is less than 13 the chief gaseous product 18 NO (Lunge, B 11, 1229, 1641)

Combinations -1 With water, it is still undecided whether a hydrate or hydrates of HNO₃ are produced when HNO₃ is dissolved in water, v Properties, p 519—2 With ammonia to form NH₄NO₃—3 With dry sulphur dioxide to form SO2 NO2 OH (v NITROGEN DERIVATIVES OF SULPHUR ACIDS in vol iv) -4 With some ni trates to form acid salts, according to Ditte (A Ch [5] 18, 320), the nitrates which combine with HNO, when dissolved in excess of the acid are those of NH, K, Rb, and Tl -5 With nitric anhydride to form $(HNO_3)_2N_2O_5$ (= $H_2N_4O_{11}$, v Dinitric acid, infra)

Detection and Estimation v Manuals of Analysis

DINITRIC $H_2N_4O_{11} (= (HNO_8)_2 N_2O_8)$ ACID Weber (J pr [2] 6, 342) obtained this compound by adding very conc colourless HNO, to melted N₂O₅, and cooling to c 8° (for details of preparation v Weber, lc) A bluish yellow liquid, so lidifying at c 5°, S G 1 642 at 18° Fumes in air, dissolves in water with production of much heat, when gently warmed N₂O₅ is evolved It is very dangerous to keep the compound in sealed tubes as explosions generally occur Acts as a power ful oxidiser, forms NO2 derivatives with many carbon compounds The relation of this acid to nitric acid is probably similar to that of disulphonic to sulphonic acid $H_2SO_4 + SO_3 = H_2S_2O_7$, $2HNO_3 + N_2O_5 = H_2N_4O_{11}$ M M P M

2HNO₃ + N₂O₅ = H₂N₁O₁, M M P M
NITRIDES Compounds of N with one other
more positive element The term is generally applied to the binary compounds of N with B, P, Si, and the metals The metallic nitrides have for the most part the composition denoted by the formulæ RN, R, N, or R, N, R = monovalent metal They are mostly obtained by the action of ammonia on metallic oxides or chlorides; frequently also by the direct action of atmospheric

cuttogen on metals at the moment of separation; that nitrates are formed in a fertile soil from NH. from their oxides by charcoal Some metallic mitrides are also obtained by the reaction of metals or oxides of metals with hydrazoic acid, HN_s $(q \ v \ p \ 559)$ Most of them have a metallic aspect, are easily decomposed by heat, sometimes to nitrates in the soil -

salts applied to the soil The following table, taken from the article Nitrification in the first edition of this Dictionary (Supp iii p 1399), exhibits very clearly the oxidation of NH, salts

Nitrogen existing as nitrates in one million parts of drainage water.

	Plots which received no NH4 salts				Plots which received 400lbs NH, salts per acre, between March 10 and 13						
Dates on which drainage water was collected	3 and 4	5	16	17	7	10	11	12	13	14	18
February 16, 1879 April 7, 1879	3 4 3 6	87 29	4 2 3 6	3 3 2 3	3 5 39 0	5 2 45 4	4 8 41 8	4 1 25 4	3 8 29 4	4 8 33 0	4 2 40 4

with explosion, some of them, however, with stand a very high temperature without decom position Many of them are reduced to metals by strongly heating in hydrogen or ammonia gas, heated with water or hydrate of potassium they often yield metallic oxides and ammonia, they burn when heated in the air They unite with other metallic compounds, especially with metalamides The chief metallic nitrides are those of Al, Cu, Cr, Fe, Mg, Hg, Mo, Ni, Nb, Pt, K, Na, Ta, Th, 9 Sn, Ti, W, U, Y, Zn, and Zr For descriptions of the nitrides v the several metals enumerated above MMPM

NITRIFICATION Nitre occurs in many parts of the earth In some places at as found as an efflorescence on the surface of the soil, it is formed on the sides of caves (generally those frequented by animals), on the walls of old stables, and in the soil surrounding some of the villages in North India (v. Palmer, C J [2] Nitre also occurs in Algeria, Spain, 6, 318) &c , and very large deposits of NaNO3 are found in Peru Nitrates are found in all, or almost all, soils, especially in those which are fertile and well manured Nitrates are obtained by the artificial oxidation of nitrogenous matters in soils, by arranging the conditions so that there is first an accumulation of nitrogenous compounds, and then a slow oxidation in presence of moisture and some base which combines with the HNO, as it is produced (v Potassium nitrate, Formation, p 515)

That HNO, is formed by the oxidation of nitrogen compounds has been abundantly proved (e g by Boussingault, C R 82, 477) There is no convincing experimental proof that the N of the air is oxidised to HNO, under normal naturally occurring conditions. L T Wright (C J 35, 42) found that HNO, is formed by burning H in air, but that if special precautions are taken to remove all NH, from the air, HNO, is not formed Bous singault (C R 76, 22) found that there was no increase in the total N in a quantity of soil rich in N compounds, after keeping in a closed vessel full of air for 11 years, although there was a marked increase in the nitrates in the soil Various experimenters have proved that NH, can be oxidised to HNO, eg by ozone, by KMnO, and H₂SO, &c (v Nitrio ACID, Formation, p 518) Experiments conducted at Rothamsted have proved conclusively

In 1862, Pasteur suggested that the oxidation of nitrogen compounds in the soil to nitrates is accomplished by a living organism In 1877 Schloesing a Muntz (C R 84, 301, 85, 1018) showed that nitrification did not take place in sewage slowly filtered through a column of pure sand and limestone until after 20 days, that nitrification then proceeded rapidly, but was completely stopped by allowing vapour of chloro form free access to the surface of the sand and limestone, 7 weeks after the application of CHCl,, a little vegetable earth, which was known to nitrify easily, was placed on the surface of the sand, and then nitrification began again S a M also showed that heating soil to 100° destroyed the power of that soil to produce nitrates from nitrogenous matter

Warington has conducted, at Rothamsted. an extensive, laborious, and accurate, series of experiments on nitrification in soils, his memoirs are to be found in C J 33, 44, 35, 429, 45, 637 [numerous references here to other workers], 47,758,51,118,53,751, cf also Munro, C J 49,632 The results fully confirm the view that the production of nitrates in soils from nitrogenous compounds is due to the ac-tivity of a living organism. Summarising the results, Warington says (C J 45, 461) 'Nitrification in soils and waters is found to be strictly limited to the range of temperature to which the vital activity of low organisms is confined Nitrification is also dependent on the presence of plant-food suitable to organisms of low character Further proof is afforded by the fact that antiseptics are fatal to nitrification action of heat is equally confirmatory raising sewage or soil to the temperature of boiling water, its nitrifying power is entirely destroyed Finally, nitrification can be started in boiled sewage, or in other sterilised liquids of suitable composition, by the addition of a few particles of surface soil, or a few drops of a solution which has lately nitrified, while, if no such addition is made, these liquids may be freely exposed to filtered air without nitrification takıng place Schloesing has apparently given a final blow to the theory that air exists in a condensed state in the pores of a soil, and may on that account exert special oxidising powers, by his recent experiments (Ann de la Science agronomique, 1884 1), showing that the gases in a vegetable soil simply occupy the normal

volume due to temperature and atmospheric pressure

The result of Warington's examination of the classes of bodies that undergo intrification in soils is, that all introgenous substances which yield ammonia by the action of organisms existing in fertile soils are intrifiable (C J 45,658)

The conditions under which nitrification proceeds in soils, sewage, &c, are as follows (W. C J 45, 654 et eq) -(1) A sufficient quantity of some base must be present to combine with the nitric acid When the whole of the bases present are neutralised the nitrification stops, although nitrifiable compounds may still be pre-There is a limit to the quantity of alkaline carbonate which can be present in a liquid undergoing nitrification This fact renders impossible the nitrification of urine, except when diluted with water, because the first product of the action on urine of organisms in the soil is NH, carbonate, and unless this be present in very moderate quantity nitrification cannot proceed Warington's experiments showed that 14 parts urine in 100 water did not nitrify when kept in contact with soil containing nitrifying organisms for 172 days Addition of gypsum allows nitrification to proceed in cases where it would either not occur or be stopped by the presence of NH₄ carbonate (W, C J 47, 758, Pickard, Ann de Science agronomique, 1884 302, Joulie, ibid 1884 289) Thus, whereas a 14 p c urine solution did not nitrify after 172 days, a 80 p c solution, to which gypsum was added, nitrified after 78 days, and a 50 p c solution containing gypsum nitrified after 151 days (2) In order that a nitrogenous liquid shall nitrify, the concentration of the liquid must not exceed a certain degree (for experiments v C J 45, 662) (3) A sufficient quantity of the nitrifying organism must be present. The vigour of the organisms obtained in different cultivations differs considerably A liquid which refuses to nitrify when seeded, because its concentration is excessive, may be caused to undergo nitrification by seeding it with a very vigorous organism, is one which has been obtained by cultivation in a fairly cone solution well supplied with nutri-ment 'The plan that has proved most effective in producing rapid nitrification is to make use of the sediment lying at the bottom of the vessel in which the nitrification of a fairly strong solution has been conducted (W, lc p 665) (4) Stagnant liquids of considerable depth nitrify much less quickly than a shallow liquid of similar composition, or than a liquid which is poured over a porous solid and so brought into contact with fresh supplies of oxygen (5) Some quantity of carbon in combination—'organic carbon'—is needed for the nourishment of the nitrifying organism, but no advantage accrues from the presence of more C than is required for this purpose (cf Munro, C J 49, 651 et seq) (6) Nitrification proceeds within certain limits of temperature, the organism seems to be destroyed at, or somewhat below, 100°, at 8°-5° nitrification proceeds much more slowly than at somewhat higher temperatures (7) Light tends to decrease, or even stop, the process of nitrifica-tion ($v \ W$, $C \ J \ 88,44$) The product of nitrification is sometimes a nitrite, sometimes a nitrate, and sometimes both The exact con-

ditions under which nitrite and nitrate are formed have not yet been determined satisfactorily. In a later communication (C J 59, 484) Warington describes the isolation of two organisms one of these exidises ammonia to nitrous acid and has no effect on nitrites, the other produces neither nitrites nor nitrates in ammoniacal solutions, but in absence of ammonia rapidly converts nitrites into nitrates P F Frankland and G C Frankland (Pr 47, 296) seem to have isolated a bacillus, which grows slowly in broth, and which converts ammoniacid salts into nitrates.

With regard to the distribution of the nitrifying organisms in the soil, Warington's experiments show that the organisms are not evenly distributed below a depth of about 9 inches in clay-soils ($C\ J\ 45,649$), and that nitrification occurs chiefly, if not altogether, in the surface soil, and rarely in a clay-subsoil 2 or 3 feet from the surface ($C\ J\ 51,118$) M M P M

NITRILES Compounds of the form RCN

where R is an organic radicle

Formation —1 By distilling potassium alkyl sulphates (KRSO₄) with potassium eyanide (Dumas, C R 25, 474) —2 From alkyl iodides and potassium cyanide in presence of dilute alcohol (Schlagdenhauffen, C R 48, 228, Henry, C R 104, 1181) —3 By dehydrating amides by distillation with P₂O₅ or P₂S₅ (Dumas, Malaguti, a Leblanc, A 64, 333) —4 By distilling organic acids with potassium or lead sulphocyanide This reaction is most successful with aromatic acids (Kruss, B 17, 1766) -5 By boiling the formyl derivatives of aromatic amines (e.g. (formanilide) with zinc dust (Gasiorowski, B17,73) -6 By the action of bromine and NaOH on the amide of the acid containing one C X CH₂ CONH₂ + 3Br₂ + 8NaOH atom more $= X CN + 6NaBr + Na_2CO_3 + 6H_2O$ This reaction, which gives a means of descending the series, is particularly applicable to the higher homologues (yield from monoamide = 30 pc), but the lower the homologue the smaller is the yield, till in the case of valeramide hardly any nitrile at all is formed, the chief product of the reaction being butylamine (Hofmann, B 17, 1406) —7 By distilling the formyl derivatives of aromatic monamines with zinc dust, the yield being 10 pc-20 pc (Gasiorowski a Merz, B 18, 1008) -8 By warming the oxim of the corre sponding aldehyde with Ac₂O -9 Aromatic nitriles may be formed from diazo- compounds by Sandmeyer's reaction, using cuprous cyanide (Šandmeyer, B 17, 2653)

Reactions —1 Readily converted into NH,

Reactions—I Readily converted into NH, and the corresponding and by heating with acuds or alkalis Cold cone HClAq forms the intermediate amides—2 Alcohol (1 mol) and gaseous HCl form the salt of an imido-ether, e.g. CH, CH(OEt) NH,Cl.—3 Zinc and dilute acids yield the corresponding amine (Mendius, A 121, 129)—4 H.S unites, forming a thio-amide, e.g. CH, CS NH, —5 Sodium polymerises many fatty nitriles—Sodium acting on an alcoholic solution of aromatic nitriles often reduces them to the aromatic hydrocarbons or their hydrides (Bamberger a Lodter, B 20, 1702)—6 HBr combines with nitriles—The product is decomposed by water, fatty nitriles yielding the acid, while benzomitrile yields benzamide—

7 Hydroxylamins unites, forming amidoxims BC(NH2) NOH

Isonitriles v. Carbamines
NITRILO DIACETONAMINE v. ACETOM-

NITRILO - PROPIONITRILE A name for hydrocyanaldine v vol 1 p 104

NITRILES Salts of nitrous acid, HNO2, v. Netrous acid and Netrites, under Nithogen, p 567

NITRO-Use of this prefix applied to inorganic compounds for nitro-compounds and nitro salts v the element the nitro compound of which is sought for, or the salts to the names of which nitro is prefixed Thus, nitroferrocyanides are described under ferrocyanides, a section of the group Cyanides, nitrochromate of potassium is described under Chromates

NITRO-ACENAPHTHENE C₁₂H₂NO₂. [155°] (J), [102°] (A) Formed by nitrating acenaphthene dissolved in HOAc (Jandrier, C R 104, 1858, Quincke, B 20, 609, 21, 1454) Paleyellow needles (by sublimation) Easily reduced by zine and HCl to an amido derivative, which yields a bluish-violet product on oxidation

Dinitro-acenaphthene $C_{12}H_8(NO_2)_2$. [206°] Yellow needles, formed at the same time as the

preceding (Q, cf Berthelot, Bl 8, 250) NITRO ACETIC ACID CH₂(NO₂)CO₂H or

 $CH_2(ONO)CO_2H$

Ethyl ether EtA' (c 155°) SG 21133 Formed from bromo or iodo acetic ether and silver nitrite at 130° Extracted with ether Extracted with ether Forerand, Bl [2] 31, 536, Steiner, B 15, 1605, Lewkowitsch, J pr [2] 20, 163) Oil, smelling like nitrous ether Yields amido acetic ether on reduction Splits up when boiled for a long time, yielding CO2, oxalic ether, and NO

NITROACETAMIDO-DI METHYL-HYDRO-QUINONE v Acetyl-di methyl derivative of

NITRO AMIDO-HYDROQUINONE

NITRO ACET ANILINE v Acetyl derivative of Nitro aniline

NIIRO-ACET-NAPHTHALIDE v Acetyl derivative of NITBO NAPHTHYLAMINE

NITRO ACETONITRILE A name formerly given to fulminic acid (v vol 11 p 817)

NITRO ACETONYL-UREA

 $CMe_2 < CO NH CO > (?)$ [141°] Obtained by nitrating acetonyl urea (Franchimont a Klobbie, R T C 7, 241) Slender needles, sl sol water and benzene, sol alcohol and ether Decomposed by boiling water, forming a oxy-isobutyric acid

o NITRO-ACETOPHENONE C,H,NO, 1e CH, CO C, H, NO, [1 2] Nitro phenyl methyl ketone Formed, together with the m-isomeride, by nitration of acetophenone, especially at 40° (Engler, B 18, 2238) Prepared by boiling o nitro-benzoyl-acetoacetic ether with dilute H.SO. for 8 hours, and extracting with ether (Guthzeit, A 221, 325) Oil, v sol alcohol With PCl, it yields chloro-o-nitro-styrene Boiling alcoholic ammonium sulphide converts it into indigo KMnO, yields o-nitro benzoic acid Tin a HCl yield o-amido-acetophenone (242°-252°). Tm and

m Nitro-aceto-phenone CH, CO C, H, NO, [18] [81°] (Buchks, B 10, 1714) Formed by the action of m nitro-benzoyl chloride on sodio acetacetic ether and digesting the product with water (Gevekoht, B 15, 2084)

Obtained also by nitrating acetophenone in the cold Needles, volatile with steam nitro-benzoic acid on oxidation

Oxim [132°] F (Gabriel, B 15, 3063) Forms a methyl-ether [64°]

p-Nitro-acetophenone CH, CO C,H,NO, [1:4].
[81°] Formed by the action of Tourish Formed by the action of p nitro-benzoyl chloride on sodio acetacetic ether, and digesting the product with water (Gevekoht, B 15, 2084) Formed also by warming p-nitro phenyl-propiolic acid with dilute H2SO, or by allowing its ether to stand with cone H2SO4 at 40°, pouring the p nitro-benzoyl acetic acid which is formed into water, and expelling CO, by boiling (Drewson, A 212, 160, Engler a Zulke, B 22, 203) Yellow prisms Yields chloro-p-nitro-styrene with Pol, Yields p-amido acetophenone [106°] Yields chloro-p-nitro-styrene on reduction by tin and HCl.

Phenyl-hydraside CH₂C(N₂HPb) C₆H₄NO₂ [132°] NI1RO-ACET TOLUIDE v Acetyl derevatwe of NITBO TOLUIDINE

NITRO ACET-XYLIDE v. Acetyl derivative of Niteo xylidine

DI-NITRO-ACETYLENE-DI-UREA C,N,H,O, Le CO NH C(NO.) NH CO Di-nitroglucol-

urile Formed by nitrating acetylene-di-urea (Franchimont a Klobbie, R T C 7, 18) Chars at 180° On boiling with water it is decomposed into CO₂, water, and an isomeride of hydantoïc acid. NITRO- ACIDS v. Nitro- compounds

(a)-NITRO-ACRIDINE $C_{12}H_2N_2O_2$ 2 6. $C_{12}H_4(NO_2)N$ [214°] Formed, together with the two following bodies, by nitrating acridine (Graebe a Caro, A 158, 275) Golden-yellow plates (by sublimation), insol water, sl sol. alcohol and ether Its solution in dilute acids

The hydrochloride shows blue fluorescence crystallises in yellow prisms

Plates, v sol. hot (β) Nitro-acridine [154°] alcohol Forms salts with acids

Di-nitro acridine C₁₂H₇(NO₂)₂N. Reddishyellow tables, sl sol alcohol and ether not dissolve in dilute acids

TRI NITRO ACRIDINE CARBOXYLIC ACID O18H5(NO2)3NCO2H Formed by boiling methylacridine with HNO, (SG 133) (Bernthsen, A. 224, 40) Yellow prisms

NITRO ALDEHYDO BENZOIC ACID C₆H₃(CHO)(NO₂) CO₂H [1 2 4] [160]

Formed, together with a small quantity of $C_0H_3(OHO)(NO_2)CO_2H$ [1 3 4] [184°] by nitrating p aldehydo benzoic acid (Löw, A 231, 368) Four sided prisms (from water), v sol alcohol and ether With acctone and NaOH it forms ındıgo carboxylıc acıd —AgA' al sol water

Ethyl ether EtA'

NITRO ALDEHYDO-CINNAMIC ACID C₁₀H,NO₅ 4.6 C₆H₅(CH CH CO₂H)(NO₂)(CHO) [1 2 4] [194°]. Formed by nitration of aldehydocinnamic acid (Low, A 231, 376) Prisms sol glacial acetic acid, acetone, and hot water, hardly sol. ether or chloroform Does not give the indigo reaction with acetoms and NaOH, so that NO, is probably not ortho to CHO -AgA' aq.

Ethyl ether EtA' [80°] Prisms
NITRO ALIZARIN v NITRO-DI-OXY ANTHRA-

DI NITRO ALLYL-ANILINE C.H.N.O. ... C.H.NHC.H.(NO.).. [76°] Formed from bromom di nitro-benzene, allylamine, and alcohol (Romburgh, R T. C. 4, 192) Yellow needles

mburgh, A 2.0. 7, 100 The No. 10 to Tri-nitro-allyl-aniline C.H.N.O. 10 to PNHCH (NO.). [80°] Formed by the C.H.NHC.H.(NO.). [80°] Formed by the action of allylamine on chloro tri nitro benzene (picryl chloride) (R)

p-NITEO-ALLYL-BENZOYL-ACETIC ETHER C.H.(NO.) CO CH(C.H.) CO.Et [46°] Formed (from sodium p nitro benzoyl acetic ether and

allyl modide (Perkin a Bellenot, C J 49, 452) NITEO-AMIDO-ACETAMIDE C.H.N.O. 10 CH2(NH NO2) CONH2 Formed by decomposing nitro hydantoin by boiling water (Franchimont a Klobbie, R T C 7, 239) Long prisms, decomposing at 180°

NITRO . DI . AMIDO . BENZENE v NITRO-PHENYLENE DIAMINE

NITRO - AMIDO - BENZENE SULPHONIC $\textbf{ACID} \quad \textbf{C}_{e}\textbf{H}_{e}\textbf{N}_{2}\textbf{SO}_{5} \quad \textbf{1} \ \textbf{e} \quad \textbf{C}_{e}\textbf{H}_{3}(\textbf{NO}_{2})(\textbf{NH}_{2})(\textbf{SO}_{3}\textbf{H})$ [2 1 4] o Nitraniline sulphonic acid Formed by heating (1, 2, 4) bromo nitro benzene sulphonic acid with alcoholic NH, at 180° (Goslich, A 180, 103) and by nitrating acetyl p amido benzene sulphonic acid (Nietzki, B 18, 294, 21, 3220). The same acid appears to be formed by sulphonating o-nitro aniline (Post a Hardtung, B 13, 38) Yellow needles, extremely sol water, m sol alcohol and HClAq Boiling aqueous KOH converts it into C₈H₃(NO₂)(OK)(SO₃K) Boiling aqueous

AOH converts it into C₆H₃(NO₂)(OK)(SO₂K)
HClAq at 180° yields o-mitro amline

Salts — KA'aq S 5 at 6° — NH₄A' S 18
at 6° — BaA', 24aq S 5 at 9° — CaA', 24aq
(P a H) — PbA', 2aq S 2 at 6°

Chlorade C₆H₂(NO₂)(NH₂) SO₂Cl [60°]

Amade [156°] Yellow needles

Nitro-amido-benzene sulphonic acid

 $C_6H_3(NO_2)(NH_2)(SO_3H)[1\ 2\ 4]$ Formed by the action of HNO, (1 mol) on acetyl amido benzene m-sulphonic acid (1 mol) dissolved in conc H₂SO₄ (Eger, B 21, 2579, 22, 847) Yellow needles (from water), sl sol alcohol, almost insol ether —KA' golden yellow plates (from water) —NaA' yellow needles, v sol water Witro-amido-benzene sulphonic acid

heating m-introamline sulphate at 120°-170° with CISO,H (Limpricht, B 18, 2186) Long colourless prigns or cluster 18. colourless prisms or glistening plates soluble in hot water, more sparingly in cold

Salts —A'K aq long thin glistening red prisms or yellowish-red plates —A'Na 2aq small yellow plates —A'₂Ca 4aq easily soluble large orange tables or thick red prisms -Ă'₂Ba aq red tablets or prisms, sparingly soluble in cold water

Nitro-amido-benzene sulphonic acid ${}^{\mathbf{C_6H_2(NO_2)(NH_2)(SO_2H)[3\ 1\ 4]}}$? Formed by heating m nitro aniline with fuming H₂SO₄ at 160° (Post a Hardtung, A 205, 102, B 18, 40)
Yellowish-brown prisms — Bah' 2aq long
spikes S 14 at 100° — Cah', 4aq small
needles, v sol water This acid is perhaps identical with the preceding

Nitro-amido-benzene sulphonic acid C₅H₄(NO₂)(NH₂)(SO₅H)[4 1 3] Formed in small quantity by heating O₅H₄Br(NO₂)(SO₂H) [1 4 3] with alcoholic ammonia at 160° (Thomas, A 186, 132) Needles, v. sol water —BaA'₂ 1½aq 15 at 15°

Nitro-amido-benzene disulphonic acid C₂H₂(NO₂)(NH₂)(SO₂H)₂. Formed by the action

of ammonium sulphide on di nitro benzene disulphonic acid obtained from nitro benzene m sulphonic acid (Limpricht, B 8, 289) Very deliquescent mass—BaA" 2aq

(a)-NITRO-AMIDO-BENZOIC ACID $C_rH_sN_2O_s$ is $C_sH_s(NO_s)(NH_s)$ $CO_rH[2\ 5\ 1]$. Mol w 182 Formed by boiling (a) di nitrom-uramido benzoic acid with water (Griess, B 5, 198, 11, 1734) Yellow needles or prisms, m sol hot water, v sol hot alcohol Yields nitro oxy benzoic acid [169°] Yields on reduction a diamido benzoic acid which forms p phenylene-diamine on distillation —BaA', 3aq (β) -Nitro-amido-benzoic acid

 $C_6H_3(NO_2)(NH_2)CO_2H[4\ 3\ 1]$ [298°] Formed by boiling (β) di nitro m uramido benzoic acid with water (Griess) Formed also by saponifying its acetyl derivative (Kaiser, B 18, 2946) Red plates or needles Yields on reduction a diamido benzoic acid which forms o phenylenediamine on distillation - CaA', aq red crystals,

sl sol water —BaA'₂ 2aq Ethylether EtA' [139°] Red needles Formyl derivative [221°] (Zehra, B 28, 3634)

Acetyl derivative $C_6H_3(NO_2)(NHAc)CO_2H$ [206°] Formed, together with the (2, 3, 1) isomeride, by nitrating m acetamido benzoic acid below 0° (K) Yellow $tables - CaA'_2 7\frac{1}{2}aq - BaA'_2 7aq$

γ-Nitro-amido-benzoic acid $C_{e}H_{s}(NO_{2})(NH_{2})(CO_{2}H)[2\ 3\ 1]$ [157°] Formed by boiling (γ) di nitro m uramido benzoic acid with water (Griess, B 2, 435, 5, 199) Formed also by saponifying its acetyl derivative which is prepared as above (K) Long yellow needles, v sol hot water Yields o nitro benzoic acid on elimination of NH₂ (Griess, B 11, 1734) Yields on reduction a di amido benzoic acid which forms o phenylene diamine on distillation —KA'2aq —BaA', 7aq —HA'HCl, crystals, decomposed by water

Acetyl derivative C₆H₂(NO₂)(NHAc) CO₂H [24] crystals — CaA'₂ 6aq — BaA'₂ aq [241°] Colourless (δ) -Nitro amido benzoio acid

 $C_6H_2(NO_2)(NH_2)CO_2H[341]$ [284°] Formed by heating di-nitro-p uramido benzoic acid with water (Griess, B 5,855) Formed also by heating C₆H₃(NO₂)(OMe) CO₂H [3 4 1] with aqueous ammonia at 140°-170° (H Salkowski, A 173, Reddish yellow needles (from alcohol), sl sol hot water Yields, on reduction, di amido benzoic acid [210°] Converted into m nitro

benzoic acid by the diazo reaction —KA'aq orange prisms —BaA', 5aq

Ethyl ether EtA' [145°] Formed by heating C₈H₂Br(NO₂) CO₂Et [4 3 1] with alcoholic NH, for 3 hours at 150° (Grohmann, B 23,

3449) Yellow crystals
Amide C₆H₂(NO₂)(NH₂) CONH₂ [227°]
Formed by heating C₆H₂Br(NO₂) CONH [4 3 1] crystals, insol water, sl sol alcohol

Acetyl derivative C₆H₂(NO₂)(NHA₀) CO₂H [221°] Formed by nitration of acetyl p amido benzoic acid below 10° (Kaiser, B 18, 2948) Thick yellow tables, v. sl sol cold water —CaA'₂ 2aq —BaA'₂ 6 aq (e)-Nitro-amido-benzoio acid

C.H.(NO.)(NH.)(CO.H) [5 2.1] [268°].

Formation - 1 By boiling di nitro-o uramido benzoic acid with water (Griess, B 11, 1730) —2 By heating C₆H₃(NO₂)(OEt) CO₂Et with alcoholic NH₂ at 140° and boiling the resulting amide with baryta water (Hubner, A 195, 21) —3 By heating C₆H₃Br(NO₂) CO H [2 5 1] with cone NH₃Aq at 145° (Rahlis, A 198, 112) -4 From its amide which is formed when nitro isatoic acid is warmed with aqueous am

monia (Kolbe, J. pr. [2] 30, 477)

Properties — Slender yellow needles, v. solboiling water On elimination of NH₂ it yields

m nitro benzoic acid

Salts —KA'2aq — CaA'₂8aq — BaA'₂3aq v sol cold water, sl sol hot water —PbA'₂2aq — HA'HCl needles, decomposed by water

Amide CoH3(NO2)(NH2) CONH2

Yellow needles (from acetone) (5) Nitro-amido-benzoic acid

C₆H₃(NO₃)(NH₂)(CO₂H) [3 2 1] [204°] Formed by heating C₆H₃(NO₂)(Obt)(CO₂Et) [3 2 1] with alcoholic NH₃ at 130°-160° and saponifying the resulting amide (Hubner, A 195, 37) needles (from water) On elimination of NH2 it yields m nitro benzoic acid -KA' - CaA'₂ 2aq -SrA'₂ 2aq -BaA'₂ 2aq purple needles, si sol cold water - Pb(OH)A' - CuA'₂ - AgA' -HA'HCl needles

Ethyl ether EtA' [204°] Plates [109°] Amide C₆H₃(NO)(NH₂)(CONH₂) Yellow plates, almost insol water and alcohol

(η) Nitro-amido-benzoic acid

 $C_6H_3(NO_2)(NH_2)CO_2H$ [5 3 1] [208°] Formed by reducing s di nitro benzoic acid with NH, and H₂S (Hubner, A 222, 81) Small golden prisms (from water) On elimination of NH2 it yields m nitro benzoic acid Reduces to di amido benzoic acid which, when distilled with steam, forms phenylene m diamine — NaA' aq red needles -NH, A' 3aq bright yellow needles $-- BaA'_2 4aq -- CaA'_2 5 \frac{1}{2}aq -- PbA'_2 3 \frac{1}{2}aq$ AgA aq

Ethyl ether EtA' [155°] Yellow needles Di-nitro-o-amido-benzoic acid C,H,N,O, i e [256°7 $C_0H_2(NO_2)_2(NH_2)$ CO H Mol w 227 Formed, together with its methyl ether, by heating C₆H₂(NO₃) (OEt) CO₃Me with aqueous ammonia (H Salkowski, B 4, 870, A 173, 40) Golden yellow scales (from alcohol) -NH, A'aq

Methyl ether MeA' [165°] Needles Ethyl ether EtA' [135°] Laminæ

Di nitro p amido benzoic acid $C_0H_2(NO_2)_2(NH_2)(CO_2H)$ [5 3 4 1] Chrysanssc acid [260°] Formed by the action of aqueous ammonia upon C₈H₂(NO₂)₂(OMe)CO₂H, which is a product of the action of warm fuming HNO3 on anisic acid (Cahours, A Ch [3] 27, 454, Beilstein a Kellner, A 128, 104) Formed also by oxidation of di nitro p toluidine by chromic acid mixture (Friederici, B 11, 1975) Plates (from alcohol), sl sol cold Aq -NH₄A' -AgA'

Methyl ether MeA' [144°] Plates

Methyl ether MeA' [144°] Ethyl ether EtA' [114°] Plates

Acetyl derivative

C_eH₂(NO₂)₂(NHAc) CO₂H [270°] Silky needles Nitro-di-amido-benzoic acid C,H,N₃O₄ * 6 C₆H₂(NO₂)(NH₂)₂CO₂H [5 4 3 1] Formed by reducing chrysanisic acid with H₂S and alcoholic NH_a (B a K) Minute red crystals, v sol alcohol, sl sol hot water — NH₄A'aq Monochimo prisms, a b c = 1.073 1 1 809, $\beta = 77^{\circ} 32'$

DI - NITRO - AMIDO - BENZYL - METHYL KETONE C.H.N.O. [214°] Formed by reducing tri nitro benzyl methyl ketone in alco Formed by reholic solution with the theoretical quantity of SnCl₂ and HCl (Dittrich, B 23, 2724) of golden yellow needles (from alcohol)

NITRO AMIDO-ISOBÙTYL-BENZENE

C.H., C.H., (NO₂)(NH₂)[1 2 3] Netro isobutyl anrine [124°] Formed by saponifying its acetyl derivative (Gelzer, B 21, 2941) Yellow crystals, v sol boiling water

Acetyl derivative [106°] C₄H₉ C₆H₃(NO₂)(NHAc) Obtained by nitrating C.H. C.H. NHAc Yellow needles, v

sl sol boiling water

Nitro amido isobutyl benzene C_4H_9 $C_6H_3(NO_2)(NH_2)$ [1 3 4] [106 5°] Formed from its acetyl derivative and alcoholic potash (Gelzer, B 20, 3254) Orange crystals, al sol. hot water

Acetyl derivative

 C_4H_9 C_6H_3 (NO₂)(NHAc) [105°] (252°) needles Obtained from C.H. C.H. NHAc [1 4] and fuming HNO, at 0°

Di nitro amido isobutyl benzene

C₆H₂(C₄H₉)(NO₂)₂(NH₂) [127°] Got by heating direction isobutyl phenol [93°] with NH₂Aq at 175° (Barr, B 21, 1544) Yellow needles

p NITRO DI AMIDO-DI-ISOBUTYL-TRI PHÉNYL METHANE

 $C_0H_4(NO_2)$ CH($C_0H_3(NH_2)$ C₄H₉), [126°] Formed from p nitro benzoic aldehyde, p amido isobutyl benzene, and conc H2SO4 (Bischler, B 21, 3207) Yellow needles Its hydrochloride and platinochloride are both crystalline Its di acetyl derivative melts at 114°, and its di benz oyl derivative at 126°

m Nitro di p amido di isobutyl tri phenyl methane C $H_{33}N_3O$ [65°] Formed from mnitro benzoio aldehyde, p amido isobutyl benz ene, and conc H_2SO_4

Di benzoyl derivative [114°] Plates

(a) NITRO O-AMIDO CINNAMIC ACID C₉H₈N₂O₄ re C₆H₈(NH₂)(NO) CH CH CO₂H? [240°] Formed from o amido cinnamic acid (1 pt), conc H_2SO_4 (15 pts), and KNO_3 (3 pts) at 0° On dilution with water (β) nitro o amido cin namic acid separates as brownish needles, while the (a) compound may be ppd by nearly neu tralising the mother liquor with NaOH (Fried lander a Lazarus, A 229, 241) Brown needles Insol benzene, ether, or petroleum, sl sol water, sol alcohol and acetone Dissolved by mineral acids, but ppd by sodic acetate With HCl at 150° it gives (a)-nitro carbostyril (nitro oxy quinoline), which forms slender white needles, v sl sol alcohol, glacial acetic acid, or acetone, and does not melt below 320°

 $[160^{\circ}]$ Lthyl ether EtA' Formed. along with (β) nitro-carbostyril, by nitrating oamido cinnamic ether Compact brown needles

(β) Nitro-o amido cinnamic acid C₆H₃(NH₂)(NO₂) CH CH CO₂H [254] pared as above Brownish yellow needles Insol dilute mineral acids, and in water Sol alkalis With HCl at 150° it gives (β)-nitro carbo styril [260°], which crystallises from glacial acetic acid in compact yellow needles

(3 4 1)-Nitro amido cinnamic acid $C_6H_3(NO_2)(NH_2) C_2H_2 CO_2H$ [225°] Formed by saponifying its acetyl derivative, which is

formed by nitration of acetyl-p-amido cinnamic acid (Gabriel a Herzberg, B 16, 2021) Red needles Sol hot alcohol and acetic acid, less sol water, nearly msol. benzene and ligroin

Acetyl derivative [261°-266°] NITRO-AMIDO-o-CRESOL

C₆H₂Me(NO₂)(NH₂)(OH) [1 3 5 2] [118°] Obtained by nitrating C₆H₂Me(CO₂H)(NHAc)(OH) [1352] and saponifying the resulting acetyl derivative (Nietzki a Ruppert, B 23, 3478) Brownish red needles (from alcohol)

Di-acetyl derivative

C_eH₂Me(NO₂)(NHAc)(OAc) [146°] Nitro-amido-oresol Methyl ether

C.H.Me(NO.)(NH.)(OMe) [1 2 4 5]. [182°] Formed from its acetyl derivative in elimination of NH. and reduction it yields],H,Me(NH,)(OMe) [111°]],H,Me(NH,),OMe [166°] Reduction yields

Acetyl derivative)_eH₂Me(NO₂)(NHAc)(OMe) [156°] Formed rom C.H.Me(NHAc)(OMe) in HOAc by treat nent with HNO, (SG 148) (Limpach, B 22,

Needles

Nitro ω-amido cresol Methyl ether of the

icetyl derivative

J₆H₂(CH₂ NHAc)(NO₂)(OMe)[1 3 4] Methylderinative of acetyl-nitro oxy benzylamine [137°] Formed by nitrating CaH4(CH2NHAc)(OMe) in the cold (Goldschmidt a Polonowska, B 20, 2410) Prisms, v sl sol hot water Yields Prisms, v sl sol hot water ntro anisic acid on oxidation

Di-nitro amido m cresol

0.HMe(NO₂)₂(NH₂)OH [151°] (L a D), 156°] (E a O) Formed by reducing tri-nitroresol C₆HMe(NO₂)₂OH [1 2 4 6 3] with H₂S and alcoholic NH₈ (Kellner a Bellstein, A 128, 166, Liebermann a Dorp, A 163, 104, Emmerling Oppenheim, B 9, 1094) Thin yellow needles (from hot water)

Di nitro amido-m-cresol

 $O_eHMe(NO_2)_2(NH_2)(OH)$ [1 2 or 5 4 6 3] [160° Formed by nitrating C.H.Me(CO.H)(NHAc)(OH) (Nietzki a Ruppert, B 23, 3479) Large red needles Perhaps identical with the preceding

Mono-acetyl derivative
Di-acetyl derivative [1]
NITRO AMIDO ISO CYMENE [225°] [175°]

 $O_6H_2(NO_2)(NH_2)$ PrMe [x 5or6 3 1] Formed from its phthalyl derivative by heating with cone HCl for 24 hours at 180° (Kelbe a Warth, A 221, 176) Oil Volatile with steam

Bensoyl derivative C₆H₂(NO₂)(NHBz)PrMe [1779] Formed by nitration of the benzoyl derivative of amido-iso-

Phthalyl derivative

(C₃H₂(NO₂)PrMe)₂C₂O₂C₅H₄ [167°] Formed by nitration of the phthalyl derivative of amido [167°] Formed by 180 cymene

Di-nitro-amido-cymene C₆HMePr(NO₂)₂(NH₂) [1 4 2 6 8] [113°-115°] From the ethyl ether of di nitro-thymol and alcoholic NH, at 180° (Mazzara, G 19, 160) Yellow tables dilute alcohol), si sol hot water NITEO-p AMIDO-ETHYL-BENZENE Yellow tables (from

C_eH₂(C₂H₄)(NO₂)(NH₂) [1 8 4] [47°] Yellowish-red prisms Sol. alcohol, ether, benzene, ohloroform, and CS, more sparingly in ligroin acetyl compound is obtained by careful nitration of acetyl-p-amido-ethyl-benzene.

Acetyl derivative

C₅H₅(C₂H₅)(NO₂)(NHAc) · [47°], long yellow siky needles, extremely soluble in alcohol, ether,

&c, less easily in ligroin (Paucksch, B 17, 769)
Di-nitro-p-amido-ethyl-benzene
C-H₃(C₃H₃)(NO₂)NH₂[1 8 5 4] [185°] Orange-Sol benzene and chloroform, yellow prisms less easily in alcohol and ether The acetyl derivative is obtained by nitration of acetyl p amido ethyl-benzene

Acetyl derivative

 $C_8H_2(C_2H_3)(NO_2)_2NHAc$ [182°], needles

NITRO AMIDO-HYDROQUINONE Acetyl dr-methyl derrvative

 $C_sH_2(NO_2)(NHAc)(OMe)_2$ [164°], yellowneedles Formed by nitration of acetyl-amido-a methyl-hydroquinone (Baessler, B 17, 2121)

NITRO-AMIDO HYDROTOLUQUINONE

C_sHMe(NO₂)(NH₂)(OH)₂ Formed by reducing di nitro hydrotoluquinone with SnCl₂ (Kehrmann a Brasch, J pr [2] 39, 389) Its hydro chloride crystallises in long yellow needles changing to small plates

NITRO AMIDO MESITYLENE

 $C_6HMe_3(NO_2)(NH_2)$ [73°] Nitro-mesidine Formed by reducing di-nitro mesitylene with alcoholic ammonium sulphide (Maule, C J 2, 116, A 71, 137, Knecht, A 215, 98, Klobbie, R T C 6,81) —B'HCl —B'₂H.PtCl₈ —B'₈H.PO,

Acetyl derivative C.HMe,(NO,)(NHAc) [191°] [191°] Formed by nitrating acetyl mesidine (Biedermann a Ledoux, B 8, 58, Ladenburg, B 7, 1133, A 179, 163) Silky needles, m sol alcohol Feeble base

Bensoyl derivative C₅HMe₂(NO₂)(NHBz) [168 5°] Formed by nitrating benzoyl mesidine

(Schack, B 10, 1711)

Nitro-di amido mesitylene CoMes(NO2)(NH.)2 [184°] Formed, together with di nitro amido mesitylene by reduction of tri nitro mesitylene by alcoholic ammonium sulphide (Fittig, A 141, 139) Orange laminæ (from water) or monoclinic crystals (from alcohol), $a\ b\ c=1\ 625\ 1$ 417, $\beta=60^{\circ}\ 4'$ (Lang, A 141, 140, Hintze, A 235, 183), v sl sol cold water —B"H,Cl₂ tables
D1-nitro amido mesitylene C₆Me₈(NO₂),(NH)

Di nitro mesidine [194°] Formed as above Sulphur yellow crystals (from alcohol), insolwater Very feeble base, its hydrochloride being

decomposed by water

Acetyl derivative C_eMe₃(NO₂)₂(NHAc) 5°] S (alcohol) 5 at 78° Formed by [275°] nitrating the acetyl derivative of nitro amido-Needles mesitylene

NITRO AMIDO - DI - METHYL ANILINE v NITRO PHENYLENE DI-METHYL DIAMINE

TETRA NITRO DI-METHYL-DI AMIDO-DI. PHENYL-METHANE Dr-netro-derivative CH₂(C₆H₂(NO₂)₂ NMe NO₂)₂ Formed by the ac ton of HNO₁ (S G 148) on CH₂(O₆H₁NMe)₂ dissolved in HOAc (Romburgh, R T C 7, 226)
Decomposes at 218° On boiling with aqueous KOH it gives off methylamine CrO, in HOAc forms CO(C,H₂(NO₂)₂NMeH)₂. NITRO-AMIDO-METHYL-QUINOLINE

 $O_{\bullet}H_{\bullet} < N = OMe C(NO_2)$ [201°]. Formed by heating chloro-nitro-(Py 8)-methyl-quinoline with alcoholic NH, at 190° (Conrad a Limpach, B. 21, 1965). Yellow needles (from alcohol). MITRO AMIDO (a) NAPHTHOIC ACID

C₁₁H₂N₁O₂ te C₁₂H₂(NO₂)(NH₂) CO₂H [c 110°] Formed by reducing di nitro naphthoic acid [215°] with H₂S and NH₂ (Ekstrand, J pr [2] 38, 271, B 19, 1985) Needles (from water)

Nitro-amido-(8) naphthoic acid C₁₀H,(NO₂)(NH₂) CO,H [235°] Formed by reducing di nitro (β) naphthoic acid [226°] (Ekstrand, J pr [2] 42, 301) Stellate groups of small needles -HA'HCl needles

Nitro amido (a) naphthoic acid Acetyl derivative C10H₅(NO₂)(NHAc)CO₂H [259⁵] Formed by nitrating the acetyl derivative of (4'?, 1) amido naphthoic acid (Ekstrand, J pr [2] 38, 247) Yellow needles, v sol alcohol

Nitro amido-naphthoic acid $C_{10}H_5(NO_2)(NH_2)CO_2H$ [4' 1' 1] Anhydride $O_{10}H_s(NO_2)$ $\stackrel{NH}{<}$ Netro naphthostyril [300°] Formed by nitrating naphthostyril (Ekstrand, J. pr. [2] 38, 180) Orange needles (from HOAc)

Di-nitro-amido-naphthoic acid Anhydride $C_{10}H_4(NO_2)_2 <_{CO}^{NH}$ [above 290°] Formed by nitrating the preceding anhydride (E) Plates, v sl sol HOAc and alcoho

NITRO-AMIDO (a) NAPHTHOL CiaHsN2Os e C₁₀H₂(NH₂)(NO₂)OH [130°] Formed by re ducing di nitro-(a) naphthol with ammonium sulphide (Ebell, B 8, 564) Small yellowish needles, insol water, sol alcohol

Benzoyl derivative C10H B7N2O 158°7 Small red needles (from alcohol) (Hubner, A 208, 332)

Nitro di-amido (a) naphthol Tri-acetyl derivative C10H(NO)(NHAc) OAc $[235^{\circ}]$ Formed by nitrating CioH, (NHAc) OAc [280°] (Meerson, B 21, 1195) Yellow powder, yield-(Meerson, B 21, 1195) Yellow powder, yielding phthalic acid on oxidation by potassium permanganate Fuming HClAq converts it into $C_{10}H_4(NO_2)(NH_2) < N > CMe$, whence boiling di-

lute potash forms $C_{10}H_4(NO_2)(OH) < \stackrel{O}{N} > CMe$

crystallising in brown needles [163°

NITRO-AMIDO-NAPHTHOL SULPHONIC ACID C10H2N2SO6 re C10H4(NO2)(NH2)(OH)SO3H Formed by reducing di-nitro-naphthol sulphonic acid with SnCl₂ (Lauterbach, B 14, 2029) Golden yellow plates, m sol hot water alkaline solution is blood red

NITRO-AMIDO-TETRA OXY-BENZENE

C₆(NO₂)(NH₂)(OH)₄ Formed by partial reduc tion of di nitro di oxy quinone (nitranilic acid) with SnCl Small violet needles, nearly insol alcohol, ether, and benzene (Nietzki a Benckiser, B 16, 2094, 18, 500) Its alkaline solution is readily oxidised by the air to nitro amido dioxy quinone C₆(NO₂)(NH₂)(OH)₂O₂ Nitrous acid converts 1t into nitro-diazo di-oxy quinone C_e(NO₂)(N₂OH)(OH)₂O

NITRO-0 AMIDO-PHENOL C.H.N.O. t.s C.H.(NO.)(NH.) OH [6 2 1] [111°] Formed by reducing the corresponding di-nitro-phenol with ammonium sulphide (Post a Stuckenberg, A. 205, 85) Red needles, sl sol water, v col alcohol and ether Gives a dirty-green colour

with FeOl, —B',H₂SO₄ colourless pyramids
Mitro-o-amido-phenol. Methyl ether
C₂H₄(NO₂)(NH₂)(OMe) [3 2·1] [76°]. Formed

from C_eH₂(NO₂)₂(OMe) [118°] by heating with alcoholic ammonia at 190° (Bantlin, B 11, 2106) Long yellow needles.

Nitro-o-amido-phenol C_eH₂(NO₂)(NH₂) OH [421] [142°] Obtained by reducing the corresponding di-nitro-phenol with ammonium sulphide (Laurent a Gerhardt, Compt Chim 1849, 468, A 75, 68, Post a Stuckenberg, A 205, 71) Orange prisms (containing aq) melt 205, 71) Orange prisms (containing aq) meis ing at 80° to 90° or anhydrous crystallinecrusts, melting at 142°, v sol hot water, alcohol, and ether —C₄H₄KN₂O₅C₄H₄N₂O₅ dark red nodules —AgHA" brownish yellow pp (L a G)

Benzoyl derivative C₄H₄BzN₂O₅ [above

200°] Yellow needles, al sol alcohol

Nitro-bensoyl derivative [218°] Methyl ether C_eH₃(NO₂)(NH₂)(OMe) Natro anisidine Formed by reducing $C_6H_1(NO_2)_2(OMe)$ by alcoholic ammonium sulphide (Cahours, A 74, 301) Long garnet red needles, insol cold, sol boiling, water — B'HCl

B'2H2PtCl₈.—B'HBr —B'HNO₃ —B'2H2SO₄
Benzoyl derivative of the methyl ether C₆H₃(NO₂)(NHBz)(OMe) Needles (from

alcohol), m sol boiling alcohol

Ethylether C₆H₃(NO₂)(NH₂)(OEt) [97°] Formed by heating the di-ethyl ether of di nitro di oxy s di phenyl hydrazine (hydrazonitro phenetole) with conc HClAq (Andreae, J pr [2] 21, 318) Yellow needles, m sol water Yields p nitro phenetole on elimination of amidogen —B'HCl

Nitro-o amido phenol C₆H₃(NO₂)(NH₂)(OH)[5 2 1] Carbonyl deri $vative C_8H_3(NO_2) < NH > CO$

tained by nitrating carbonyl o amido phenol (Chelmicki, J pr [2] 42, 441) Long yellow Converted by boiling needles (from water) KOHAq into nitro pyrocatechin [170°

Nitro-o amido phenol. Acetyl denivative of the methylether [143°] $C_0H_3(NO_2)(NHAc)(OMe)$ Formed by A 207, 242) Yellow needles (from alcohol)
Nitro-amido-phenol [134°]. Formed by boil

ing nitrated m phenylene diamine with aqueous KOH (Barbaglia, B 7, 1259) Orange plates

MethylNitro m amido phenol ether $C_6H_3(NO_2)(NH_2)(OMe)[4 \ 3 \ 1]$ [129°] Formed by heating (4, 3, 1) di nitro anisole with alcoholic NH₃ at 190° (Bantlin, B 11, 2106) Yel low leaflets (by sublimation)

Nitro-p-amido-phenol C_eH₂(NO₂)(NH₂)(OH) [3 4 1] [148°] Got by saponifying its acetyl derivative (Hahle, J pr [2] 43, 63) Dark-red prisms, forming a violet solution in alkalis —

KA' HA'HCl plates or prisms
Di-acetyl derivative [147°] Formed from di acetyl p amido phenol and fuming HNO. Pale yellow prisms (from dilute alcohol)

Methyl ether $C_eH_1(OMe)(NO_2)(NH_2)$ So Formed in small quantity by distilling CeH, (OMe) (NO2) NMe, OH, a crystalline compound got by mixing nitro-p amido-phenol with NMe₄OH. Crystals Yields C₆H₄(OMe)(NO₄)(NHAo) and $C_aH_a(OMe)(NO_2)(NH_aOI)$

Nitro-p-amido-phenol C.H.(NO2)(NH2)OH 60] Formed by boiling its m nitro-benzoyl derivative with alkalıs (Hübner, A 210, 382) Colourless needles (containing aq) melting at 183° or anhydrous golden needles, melting at 206° -KA' 1 aq red silky needles -NaA' 2aq

-BaA', 4aq
Nitro bensoyl derivative
C₆H₁(NO₂)(NH₂)O OO C₆H₁NO₂ [225°] Formed by nitrating benzoyl-p amide phenol [228°]

Yellow needles (from HOAc)

Nitro-di-amido-phenol C,H,N,O, 26 C₆H₂(NO₂)(NH₂)₂OH[4 6 2 1] Formed by reducing pieric acid with aqueous ammonium sulphide (Griess, A 154, 202) Long dark yellow needles (containing aq) or narrow plates, al sol water and alcohol, v sl sol ether --(HA')2H2SO, 5aq yellowish needles —BaA'2 2aq ruby red needles

Nitro-di amido phenol Dibensoyl deri- $C_{a}H_{2}(NO_{2})(NHBz)_{2}OH$ [167°-170°] vatīve Formed by nitrating di benzoyl (a) diamido

phenol

Nitro-di-amido phenol Dibenzoyl derivative C₆H₂(NO)(NHBz)₂OH [201°]

Formed by nitrating (6, 2, 1) di-amido phenol (Post a Stuckenberg, A 205, 79) Long brown needles, sl sol alcohol

C.H.N.O. Di-nitro-o-amido phenol C₆H₂(NO₂)₂(NH₂)(OH)[6 4 2 1] Picramic [170°] S 14 at 22° (Darney, Am 5, 36) Picramic acid

Formation -1 By reduction of pieric acid (Wöhler, P 13, 488, Girard, A 88, 281, J1855, 535, Pugh, A 96, 83, Lea, J 1861, 637

2 By nitration of nitro o amido phenol (Stuckenberg, A 205, 75), or of benzoyl-o amido phenol (Hubner, A 210, 392)

Properties -Red needles Converted by the diazo reaction into C₆H₃Cl(NO₂)₂ [110°] The salts do not explode when struck Cyanogen passed into its alcoholic solution forms 'ethoxycarbimidamido - dinitrophenol' CoH10N4O6 (Griess, B 15, 448), a crystalline body con verted by boiling HClAq into uramidodinitro

phenol

Salts -NaA'aq S 206 at 155° Dark red crystalline crusts (Smolka, M 8, 391) -PbA'₂ red needles S 038 at 20°, 057 at 100°—MnA'₂2aq S 1025 at 19°—CoA' S 031 at 100°—NiA'₂ S 0286 at 100°—AgA'— HA'HCl reddish brown needles (Petersen, Z1868, 378) -(HA'HCl), PtCl,

Acetyl derivative C6H2(NH2)(NO2)2(OAc)

[193°] (Schiff, B 19, 849)

ether C₈H₂(NH₂)(NO₂)₂(OMe) Methyl Dark violet needles (from alcohol), insol cold Aq

Di-nitro-m-amido-phenol $C_6H_2(NO_2)_2(NH_2)(OH)[6 4 3 1]$ [225°] Formed by warming di nitro aniline with alcoholic KCy (Lippmann a Fleissner, M 7, 96) Brownishred crystals, v sl sol water Yields di nitroresorcin on warming with aqueous alkalis Its salts explode on heating — KA' — BaA', HgA', aq Di-nitro-amido-phenol C₆H₂(NO₂)₂(NH₂)(OH)

[202°] Formed by the action of aqueous NH, on (8) tri nitro-phenol (Henriques, A 215, 334)

-KA' aq

Di-nitro amido-phenol $C_{e}H_{2}(NO_{2})_{2}(NH_{2})(OH)$ [6 2 4 1] Isopioramic |

acid [170°] S 082 at 22°, 81 at 100°. Formed by heating its benzoyl derivative with HClAq (Dabney, Am. 5, 33) Yellowish browns needles (from water) —KA' bluish black crys-tals (from alcohol) Explodes when heated Yellowish brown

Benzoyl derivative C_cH₋(NO_{j)₂(NHBz)(OH) [250°] Formed by heating O_cH₃(CO₂H)(NHBz)(OH) [1 5 2] dis solved in HOAo with HNO₃ at 80° (D) Yellow plates (from alcohol) —KA'aq —BaA'₂3aq —CaA'₂43aq —PbA'₂}

Di-nitro-o-amido-phenol Bensoyl deriva tive C₆H₂(NO₂) (NHBz) OH [4 3? 2 1] [220°] Formed by nitrating benzoyl o amidophenol in HOAc at -4° (Hubner, A 210, 387) Greenish yellow needles, insol water On treatment with POCl₃ it yields $C_8H_2(NO_2)_2 < N > C C_8H_3$ [219°]

-KA'2aq $-NH_4A'aq$ $-BaA'_25aq$ $-ZnA'_23aq$. -AgA' red needles

Di nitro-o-amido phenol Acetyl deriva $tive of the methyl ether C_6H_2(NO_2)_2(NHAc)(OMe)$ [157°] Formed by nitration of o acetanisidine (Muhlhauser, B 13, 921, A 207, 234) Prisms

Tri nitro-amido-phenol EthylC_bH(NO₂)₃(NH₂)(OEt) Formed by heating C_bH(NO₂)₃(OEt) NHCO₂Et with dilute H SO₄ Kohler, J pr [2] 29, 283) Small yellow needles (from alcohol)

o NITRO-p-AMIDO-DIPHENYL C₁₂H₁₀N O, 28 C₆H₄(NO₂) C₆H₄NH₂ [98°] Formed by re ducing op di nitro diphenyl with ammonium sulphide (Schultz, A 174, 225, 207, 350) Reddish brown monoclinic crystals, a b c = 1 52 1 2 19, $\beta = 69^{\circ} 31' - B'HC'$ needles

p Nitro p-amido diphenyl $C_6H_1(NO_2)$ C_6H_4 NH_2 [198°] [198°] Formed by reducing pp di nitro diphenyl with alcoholic am monium sulphide in the cold (Fittig, A 124, 278, Schultz, A 174, 222) Small red needles (from Gives p-nitro benzoic acid on oxida tion -B' H PtCl

Nitro p amido diphenyl Benzoyl deri $vative \ \tilde{C}_sH_s C_sH_s(NO)(NHBz)[1 3 4]$ [143°] Formed by nitrating benzoyl p amido diphenvl (Hubner, A 209, 339) Needles (from HOAc) Reduced by tin and HOAc to

 $C_6H_5C_6H_3 < N_H > CC_6H_5$ [198°]

Di nitro-p amido diphenyl Benzoyl deri vative C₁, H₁(NO₂)₂NHBz [206°] Formed by nitrating benzoyl p amido diphenyl (Hubner) Dark yellow needles (from HOAc)

Nitro-di-amido-diphenyl [4 1] $C_6H_4(NH_2)$ $C_6H_3(NO_2)(NH_2)$ [1 2 4] [143°] Formed by mixing benzidine sulphate (28 g) in H.SO. (300 g) with KNO. (10 g) (Tauber, B 23, Long red needles —B"H2SO, 12aq

Di-nitro di-p amido-diphenyl C12H10N4O4 1 e $C_6H_3(NO_2)NH_2[1\ 3\ 4]$

Di-nitro benzidine C₆H₃(NO₂)NH₂[1 3 4] [221°] Formed by nitration of di acetyl benz idine and saponification of the product with KOH (Brunner a Witt, B 20, 1024, cf. Strakosch, B 5, 237) Obtained also by hydro lysis of di nitro di phthalyl benzidine (Ban drowski, M 8, 471) Red needles Sol phenol, v sl sol alcohol, insol water Its tetrazo compound combines with α -naphthylamine psulphonic acid to form a dye stuff, which dyes unmordanted cotton the shade of alizarineviolet. By SnCl₂ and HCl 1t 1s reduced to tetraamido diphenyl

Di-acetyl derivative [above 300°] Di-nitro-di-p-amido-diphenyl [197°]. tained, together with the preceding, by hydrolysis of di nitro di phthalyl-benzidine Yellow needles (from alcohol) drowski)

Di-nitro-di-amido-diphenyl [4 8 1] C₈H₃(NH₂)(NO₂) C₈H₃(NO₂)(NH₃)[1 20r3 4] Di nitro benzidine [214°] Formed by stirring KNO₃ (20 2g) into benzidine sulphate (28 2g) dissolved in H₂SO₄ (300 g) (Tauber, B 23, 795) Yellow plates (from alcohol) pounds do not dye cotton Its azo com-

NITRO-AMIDO-PHENYL-ACETIC ACID $C_8H_8N_2O_4$ te $C_8H_3(NO_2)(NH_2)$ CH CO H [2 4 1] [186°] Formed by reducing (4,2,1) di nitrophenyl acetic acid with aqueous ammonium sulphide (Gabriel a Meyer, B 14, 824) Reddish yellow needles, v sol hot water and alcohol, sl sol ether ol ether Forms salts with acids and bases -HA'HCl colourless needles

[94°] Methyl ether MeA'

Ethyl ether EtA' [100°] Yellow needles

Nitro-amido-phenyl-acetic acid

 $C_6H_3(NO_2)(NH_2)\bar{C}H_2\,\bar{C}O_2H\,[3\,4\,1]$ [144°] Pre pared by saponification of its nitrile (nitro amido benzyl cyanide) by boiling with HCl (Gabriel, B 15, 836) Orange-yellow plates or needles Sol alcohol and ether, insol CS₂ By the action of amyl nitrite and HCl it gives (3,4,1) nitro diazo-• nitroso toluene C₆H₂(N₂Cl)(NO)(CH NO)

Netrile C₆H₃(NO₂)(NH) CH CN Formed by saponifying its acetyl derivative with potash Orange plates, sol water and alcohol

Acetyl derivative of the nitrile C₆H₃(NO₂)(NHAc) CH CN [113°] Formed by nitrating C.H. (NHAc) CH, CN (Gabriel) Flat vellow needles or plates, sol alcohol and hot water

m-Nitro-a amido-phenyl-acetic acid C.H.(NO.) CH(NH2) CO.H [172°] Formed by adding HNO, (1 mol) to a cold solution of aamido phenyl acetic acid in H2SO, (Plochl a Loé, B 18, 1179) Silky needles, v sol hot water, insol alcohol —CuA'₂ pale blue needles DI-NITRO-AMIDO-DIPHENYLAMINE

C12H10N4O4 2 e

[4 1] $C_6H_4(NH_2)$ NH $C_6H_3(NO_2)_2$ [1 2 4] Formed by the action of chloro di nitro benzene on p phenylene diamine in alcoholic solution in presence of NaOAc (Nietzki, B 23, 1852) Brownish red plates, sl so B'C₆H₂(NO₂),0H brown needles sol alcohol -

Acetyl derivative C12H2AcN4O4

Red needles

Di nitro-amido diphenylamine [172°] Formed from m phenylene-diamine and $C_6H_3Cl(NO_1)_2$

(Leymann, B 15, 1287) NITRO - AMIDO - PHENYL - ISOBUTYRIC ACID C₁₀H₁₂N₂O₄ t ¢ C₀H₃(NO₂)(NH₂) CH₂ CHMe CO₃H [138°] Formed by reducing di-nitro isobutyric acid

with ammonium sulphide (Edeleanu, C. J. 53, 559) Bright red plates Reduced by long boiling with ammonium sulphide to the compound

14 C.H.(NH.) CH. CHMe [216°]

NITRO - O AMIDO-PHENYL-CARBAMIC C₆H₄(NO₂)(NH₂) NH.CO₂Et [4 2 1] Vor. III

[162°] Formed by reduction of di-nitro phenylurethane with hot aqueous NH.HS (Hager, B 17, 2630) Orange red needles or prisms. sol alcohol, v sl sol water On heating above its melting point it loses EtOH, and is converted into nitro phenylene urea with the formula $C_6H_3(NO_2) < NH > CO$

NITRO - AMIDO - PHENYL - ETHANE NITRO AMIDO ETHYL BENZENE

NITRO-AMIDO DI-PHENYL-ETHYLENE C₁₄H₁₂N₂O₂ 1 e C₆H₄(NO₂) CH CH C₆H₄NH₂. [230°] Formed by reducing di nitro-di-phenylethylene with alcoholic ammonium sulphide (Strakosch, B 6, 329) Purple plates (from nitrobenzene) -B'HCl silky needles, decomposed by water

Nitro amido-di-phenyl-ethylene

[2 1] C₆H₄(NO₂) CH CH C₆H₄(NH₂)[1 2] Formed by reducing dionitro stilbene, formed by the action of alcoholic potash on o nitro benzyl chloride (Bischoff, B 21, 2077) Amorphous mass, sol ether and alcohol

Di-nitro-amido phenyl ethylene v Di nitro-

AMIDO STYRENE

p NITRO - DI-p-AMIDO-TRI - PHENYL -**METHANE** $C_6H_4(NO_2)$ $CH(C_6H_4NH_2)_2$. Prepared by heating aniline sulphate (28 pts) with p-nitro benzoic aldehyde (15 pts) and ZnCl₂ (20 pts) at 100° (Fischer, B 15, 677) Large Yields garnet red crystals (containing C, Ha) paraleucaniline on reduction with zinc and HCl -B"H2Cl2 needles

m Nitro-di-p amido-tri-phenyl-methane [3 1] $C_6H_4(NO_2)$ $CH(C_0H_4NH_2[14])_2$. [136°] Prepared by heating m nitro benzoic aldehyde with aniline hydrochloride and ZnCl2 (Fischer a Ziegler, B 13, 671) Light yellow crystals, sol ether Crystallises with C.H. in yellow concentric crystals [81°

NITRO AMIDO-PHENYL-(a)-NAPHTHYL-

AMINE $C_{16}H_{13}N_3O_2$ t e $C_{16}H_{7}NH$ $C_{8}H_{7}(NO_s)$ $NH_{2}[1\ 4\ 2]$ [147°] Formed by reducing di nitro phenyl (a) naphthylamine with alcoholic ammonium sulphide (Heim, B 21, 2302) Dark yellow needles (from dilute alco-Gives a dark green solution in H.SO.

Nitro-amido phenyl-(β)-naphthylamine $C_{10}H_1$ NH C_6H_1 (NO₂) NH₂ [1 4 2] [195°] Formed by reducing di nitro phenyl (β) naphthylamine (Heim, B 21, 590) Needles or prisms, m sol Dyes silk golden yellow alcohol H₂SO₄ forms a yellow solution turned green by heating

Acetyl derivative C16H12AcN3O2 [200°]

Orange red needles (from alcohol)

p NITRO-a AMIDO-PHENYL-PROPIONIC ACID C.H.ON2O, re α amido phenyl propionic acid, H,SO. and α amido phenyl propionic soid, H₂SO₄, and HNO₂ (Erlenmeyer a Lipp, A 219, 218) Fluffy white mass (from alcohol), or prisms in stars (containing laq) (from water) Sl sol alcohol, m sol water, insol ether, v sol ammonia. Neutral to litmus Bitter-sweet taste Turns brown at 220°, decomposes at 240°-245° Gives. on oxidation by chromic mixture, p-nitro-benzoic Boiled with KOH it gives off NH2-

Nitro amido-β-phenyl-propionic acid [3.4.1] C.H. (NO2) (NH2) C.H. CO.H Nitro amide

HA'HO! Needles in rosettes - CuA', 2aq

hydrocinnamic acid. [145°] Red crystals Sol water, alcohol, ether, and benzene acetyl derivative is formed by nitration of pamido \$ phenyl-propionic acid

Acetyl derivative [174°] Long yellow needles Sol alcohol and benzene, al sol cold

water and ether (Gabriel, B 15, 844)

Nitro-amido-phenyl-propionic acid [241] C.H. (NO.) (NH.) CH. CH. CO.H. [189]. Prepared by reduction of di nitro phenyl propionic acid with aqueous ammonium sulphide (Gabriel a Zimmermann, B 12, 601) Plates or flat needles Sol alcohol, ether, and acetic acid, insol CS,

Di-nitro-amido β-phenyl-propionic acid [5 3 4 1] C₆H₂(NO₂)₂(NH₂)CH₂CH₂CO₂H [194°] Formed by heating $C_0H_2(NO_2)_2(OMe)$ C.H. CO.H. with ammonia in sealed tubes at 100° (Stöhr, A 225, 87) Yellow needles, v sl sol water

Does not form salts with acids.—NH,A'-BaA', 1 1 aq Methylether MeA' [102°] [95°] Ethyl ether EtA'

DI-NÎTRO-AMIDO PHÊNYÎ-TOLYL-AMINE C,H_e(NH_e) NH C_eH_e(NO₂)₂. [184°] Formed from tolylene-diamine [99°] and C_eH_eCl(NO₂)₂ (Leymann, B 15, 1237). Red tables

Formyl derivative [157°] Acetyl derivative [164°

p-NITRO-DI-o-AMIDO-PHÉNYL-DI-TOLYL-

WETHANE C.H. (NO.) CH(C.H. NH.).
(a)-Isomeride [172°] Formed from p nitrobenzoic aldehyde, p toluidine, HClAq and alcohol (Bischler, B 20, 3302) Crystallises from benzene in needles (containing C₆H₆), v al sol cold alcohol —B"H₂PtCl₅ (β)-Isomeride [127°] Formed from p-nitro-

benzoic aldehyde, p toluidine, and conc H,SO, (Bischler, B 20, 8304) Yellow plates, v sol benzene and warm alcohol, sl sol ligroin -

B"H,Cl, - B"H,PtCl,

Di-acetyl derivative [136°] Di-bensoyl derivative [152°]

m-Nitro-di o-amido-phenyl-di-tolyl-methane

[8.1]C₆H₄(NO₂) CH(C₇H₆ NH₂)₂
(a)-Isomeride [128°] Formed by the action of HCl on a mixture of m nitro benzoic aldehyde and p-toluidine

 (\bar{B}) -Isomeride [86°] Formed from m-nitro-(Bischler, B 21, 3207) Yellowish page 801, hot sleek! Yellowish needles, v sol. hot alcohol -B"H2PtCl,

D:-acetyl dervvative [104°]
Di-bensoyl dervvative [148°].
p-Mitro-di-m-amido-phenyl-di-tolyl-methane
[4 i]C₂H₄(NO₂) CH(C₂H₂ NH₂). Prepared by heating o-toluidine sulphate with p nitro-benzoic aldehyde and ZnCl₂ at 100° (Fischer, B 15,

Small yellow crystals (containing C.H.) -- NITRO-DI-AMIDO-PHENYL-DI-XYLYL-METHANE C.H. (NO2) OH(C.H.Me2.NH2)2 [92°] Formed by condensing m nitro benzoic aldehyde with m-xylidine (Bischler, B 21, 3216). Plates —B'H.Cl. yellow plates —B'H.PtCl. Acetyl derivative [132°] Needles Bensoyl derivative [186°]

[186°]

-Witro-di-o-amido-phonyl-di-xylyl-methane O.H.(NO.) CH(C.H.Me.NH.). [90°] Formed by condensing p-nitro-benzoic aldehyde with m-xylidine by H.SO. (B) Yellow needles.— B'H.OL.-B'H.PiCL.

Ds-acetyl dersvative. [88°]

Di-bensoyl derivative [192°]. Needles. DI-NITRO-DI-AMIDO-DIPHENYL SUL-PHONIC ACID

 $C_6H_3(NO_2)(NH_2) C_6H_2(NO_2)(NH_2) SO_3H [1 3 4 5]$ Obtained from di-acetyl di amido-diphenyl sulphonic acid by nitration and saponification (Zehra, B 23, 3460) - KA'aq

Di-acetyl derivative Yellow DI-NITRO-DI-AMIDO-QUINONE Yellow needles

C₆(NO₂)₂(NH₂)₂O₂[1 4 2 5 3 6] Prepared by dissolving s di amido di-imido benzene nitrate C₆H₂(NH₂)₂(NH)₂(HNO₃)₂ (1 pt) in conc H₂SO₄ (15 to 20 pts) at about 10° On adding lumps of ice to the mixture, the compound crystallises out in dark-yellow needles. It is practically insoluble in all indifferent solvents Very weak base, whose salts are readily decomposed by water By warming with dilute KOH, ammonia is evolved, and the K salt of nitranilic acid C_s(NO₂)₂(OK)₂O₂ separates out By stannous chlor ide it is reduced to tetra amido hydroquinone C₆(NH₂₎₄(OH), [1 2 4 5 3 6] (Nietzki, B 20, 2115) NITRO-AMIDO-RESORCIN C.H. N.O. 16

C₆H₂(NO₂)(NH₂)(OH)₂ [170°] Formed by reduction of dinitro resorcin with ammonium sulphide (Benedikt & Hubl, M 2, 325) Darkbrown crystals, sl sol water, v sol alcohol .-

 B'_2H_2SO , needles

Di nitro-amido resorcin

 $C_6H(NO_2)_2(NH_2)(OH)_2$. [190°] Obtained by reducing tri nitro-resorein (styphnic acid) with alcoholic ammonium sulphide (B a H) pery leaflets, insol water, sl sol alcohol

DI-NITRO-p-AMIDO-STYRENE

C_cH₄(NO₂)(NH₂) CH CH(NO₂) Formed by nitrating p amido cinnamic acid, CO₂ being split off (Friedländer a Lazarus, A 229, 247) Slender reddish brown needles (from alcohol). Conc H₂SO₄ gives off CO₂ forming a nitro amidobenzoic aldehyde

Acetyl derivative [252°]

Di nitro-amido styrene

 $C_aH_2(NO_2)_2(NH_2)C_2H_3$ Acetyl derivative. [212°], needles, sol alcohol and acetic acid, sl sol hot water, nearly insol ether, formed by nitration of acetyl p-amido cinnamic acid (Gabriel a Herzberg, B 16, 2041)

NITRO-AMIDO-TOLUENE v NITRO TOLU-

NITRO-AMIDO-TOLUENE exo SULPHONIC ACID C₀H₂(NO₂)(NH₂) CH₂SO₃H Formed by reducing C₀H₃(NO₂)₂ CH₂SO₂H by NH, and H₂S (Mohr, A 221, 226) Needles, sol water --KA'. -BaA', 2aq

Nitro-amido toluene sulphonic acid C.H.Me(NO₂)(NH₂) SO₂H [1 2 4 5] S 17 at 11° Obtained by sulphonating (2,1,4)-nitrotoluidine (Foth, A 230, 300) Yellow needles (from water) —KA'aq —BaA'24aq

Nitro-amido-toluene sulphonic acid C.H.Me(NO2)(NH2) SO.H [1 3 2 5] Formed from acetyl-o-toluidine by successive sulphonation and nitration (Nietzki a Pollini, B 23, 138)

NITRO-AMIDO-p-TOLUIC ACID $C_{\bullet}H_{\bullet}Me(NO_{\bullet})(NH_{\bullet})\tilde{C}O_{\bullet}H$ [1 2? 8 4] [245°]_ Formed by saponifying its acetyl derivative (Niementowski, J pr [2] 40, 27) Yellow needles, sol. hot water —KÅ 2aq reddish-yellow needles Acetyl derivative [210°] Formed from acetyl-amido toluic acid and HNO, in the cold. Yellow needles, msol water

Nitro-amido toluic acid

r236°1. $C_6H_2Me(NO_2)(NH_2)CO_2H$ [1 2 4 5] Formed by heating bromo nitro-toluic acid with alcoholic NH, at 180° (Fileti a Crosa, G 18, Silky yellow needles (containing aq)

DI - NITRO - DI - AMIDO - DITOLYL [3 5 4 1] $\mathbf{C_6H_2Me(NO_2)(NH_2)} \cdot \mathbf{C_6H_2Me(NO_2)(NH_2)} \cdot [\mathbf{\tilde{1}} \cdot 3 \cdot 5 \cdot 4]$ Formed by saponifying its acetyl derivative (Gerber, B 21, 746) Garnet red needles

Di-acetyl derivative Obtained from dı amıdo-dıtolyl Crystals, decomposing at 320°

NITRO-AMIDO-XYLENE v NITRO-XYLIDINE NITRO AMIDO XYLENE SULPHONIC ACID OaH10N2SO C,HMe2(NO2)(NH2)SO3H ı e [1 3 20r5 4 6] Formed by nitration of m xylidine sulphonic acid (Sartig, A 230, 388) Slender needles (from water), sl sol cold water, insol sleohol – KA' 1½aq – BaA', 1½aq – PbA', aq

NITRO AMYLENE C,H,NO, 2 &

CH, CH(NO₂) C₃H₅ Formed from allyl 10dide

and potassium intro ethane (Gal, J 1878, 833)
Oil May be reduced to C.H., NH₂ (85°)
Nitro amylene CH₁ C(NO₂) CMe₂ [166°-170°] Formed from di methyl ethyl carbinol and conc HNO, (Haitinger, M 2, 289) Oil, sol alcohol and ether Dissolves in alkalis and gives a blue colour with KNO, and H2SO4 heating with HClAq it gives NH, hydroxylamine, and acetic acid On heating with water it yields nitro ethane and a ketone gives a yellow p

NITRO ANILIC ACID v DI NITRO DI OXY-

o NITRO ANILINE C, H, N2O2 16 C,H,(NO,) NH, [2 1] o Nitraniline Mol w

[71 5°] Formation -1 By heating o bromo nitro benzene with alcoholic NH₃ (Walker a Zincke, B 5, 114) -2 Together with p nitro-aniline by nitration of acetanilide and saponification of the

product (Körner) -3 By heating o-nitro-anisole C_sH₄(NO₂)(OMe) with ammonia at 200° (Sal-kowski, A 174, 278) —4 By reduction of o dinitro benzene (Rinne a Zincke, B 7, 1374) -5 By nitration of benzanilide and saponification of the product (Lellmann, A 221, 6)

Preparation -1 By splitting off the HSO. group from o nitro-aniline p-sulphonic acid by heating it with HCl under pressure phonic acid can be very readily prepared by sulphonation and nitration of acetanilide (Nietzki a Benckiser, B 18, 294) -2 Twelve pts of onitro phenol are heated with 20 pts of aqueous NH, (35 pc) at 160°-170° for 16 hours, the product is crystallised from water, the yield being about 60 pc of the o nitro phenol employed (Merz a Riz, B 19, 1749)

Properties - Orange needles, m sol hot water, v sol alcohol, v e sol ether Volatile with steam Does not combine with chlorinated quinones (Niemeyer, A 228, 322)

Salts -B'HCl plates Decomposed by

water into HCl and o-nitro aniline

Formyl derivative C.H.(NO.)(NHCHO). [122°] Needles (Hübner a Herff, A 209, 867). Acetyl dersvative $C_0H_4(NO_2)(NHA0).$ [93°]. Yellow plates, m sol cold water Proposayi dersvative [63°] (Smith, Am.

6, 172)

Benzoyl derivative [94°] Needles Oxalyl derivative v Oxalic ACID.

m Nitro-aniline C.H.(NO.) NH.[8 1] [114°]. (285°) S ·114 at 20°, S (alcohol) 7 05 at 20° (Carnelley a Thomson, C J 53, 786)

Formation -1 By reducing m-di nitro-benzene with H₂S and alcoholic ammonia (Hofmann a Muspratt, A 57, 204, Beilstein a Kurbatoff, A 176, 44) -2 Together with p nitroaniline by adding HNO₃ to a solution of aniline in H₂SO, (Hubner, A 208, 299)

Preparation —A solution of SnCl. (3 mols) ın alcohol saturated with HCl is slowly allowed to drop into a well cooled alcoholic solution of m-di nitro benzene (1 mol) with continual agitation (Anschutz a Heusler, B 19, 2161)

Properties -Long yellow needles Colours pine wood yellow Gives no colour with bleach.

ing powder

Reactions -1 Cyanogen passed into its alcoholic solution forms a compound with formula G.H.(NO.) NH C(NH) C(NH) C₂H₄ NO. (Senf. J pr [2] 85, 530) -2 Cyanogen vodide forms a green pp of (C₂H₄(NO₂)NH), C [286°] (Hubner, B 10, 1719) -3 Silver nitrate forms a compound (C₂H₄(NO₂)(NH₂)),AgNO, [125°] when added to its alcoholic solution (Mixter, Am 1, 230) A Chlorated 239) -4 Chlorinated quinones dissolved in benzene form dark green crystalline additive

compounds (Niemeyer, A 228, 322)
Salts — B HCl Pearly crystals, v e sol. water - B'₂H₂PtCl₈ Yellow powder, v e sol water and alcohol - B'HBr plates (Staedel a water and alcohol — B'HBr plates (Staedel a Bauer, B 19, 1940) — B'₂H₂C O, crystals Acetyl derivative C,H₄(NO₂)(NHAc)

J 53, 778, Prisms

p Nitro-anilne C.H.(NO.)(NH.) [4 1] [147°] S 077 at 20°, S (alcohol) 584 at 20° (Carnelley a Thomson, C J 53, 786) Formation—1 By nitration of the anilides

of tartaric, succinic, or acetic acid, the product being saponified (Arppe, A 90, 147, 93, 157, Hof mann, Pr 10, 589, 12, 639), the o nitro aniline, which is formed at the same time, may be re moved by steam distillation (Körner) -2 By heating [4 1]C₆H₄(NO₂)(OMe) with ammonia at 200° (Salkowski, A 174, 281) —3 By reduction of p-di nitro-benzene (Zincke a Rinne, B 7, 871)—4 By heating p chloro nitro-benzene with ammonia (Engelhardt a Latschinoff, Z. 1870, 232) -5 By heating p-nitrophenol (6 pts) with aqueous NH, (20 pts) at 190°-200° for several hours, the yield being 58 pc (Merz a. Riz, B 19, 1753).

_1 Equal volumes of HNO. Preparation . (SG 142) and H₂SO₄ are mixed and cooled. Acetanilide is gradually added as long as it will The cold solution is set aside for half dissolve an hour, then poured into water, and the nitro compound crystallized from boiling water. The nitro acetanilide is saponified by boiling NaOH, and the nitraniline crystallised from water (Meldola, C J 43, 427) -2 1 kilo of acetanilide is alowly dissolved in 4 kilos of H_2SO_4 , kept cool by standing the vessel in a stream of cold water 590 gms of HNO, of S G 1 478 (= 85 pc), or the corresponding quantity of ordinary HNO, (1•42) diluted with 1200 gms of H,SO, is then very gradually run in, taking care that the temperature does not rise above 20° After standing, the product is poured into cold water, and the yellow pp of nitracetanlide which separates is filtered off and saponified by boiling with strong HCl The yield is very satisfactory (Nölting a Collin, B 17, 262, B J Friswell, priv com)

Properties -Long monoclinic needles (from Not volatile water) May be readily sublimed with steam Weak base, its salt being decomposed by water Does not combine with chlor-inated quinones Cyanogen iodide at 120° forms (C.H.(NO2) NH),C [above 300°] (Hubner)

Salts —B'HCl —B',H2PtCl

Formyl derivative C.H.(NO2)(NHCHO) [194°] Formed from formanilide and fuming HNO, at -17° (Osborn a Mixter, Am 8, 346)

Acetyl derivative C.H.(NO2)(NHAc) [207°] Formed by nitrating acetanilide Prisms Gives p nitro phenol when boiled with conc KOHAq (Wagner, B 7, 76)

Benzoyl derivative [199°] Needles

Di nitro antline C.H.N.0, i e C.H.(NO.)2(NH.) [6 2 1] Mol w 183 S (95 pc alcohol) 52 at 12° Obt [138°] Obtained by heating the methyl or ethyl ether of c-di-nitro

phenol with aqueous ammonia (Salkowski a Rehs, B 7, 370, A 174, 273) Yellow needles Yields m-di nitro benzene on elimination of NH2

Acetyl derivative C,H,(NO2)2(NHAc)

[197°

Di-nitro aniline C₄H₄(NO₂)₂(NH₂) [4 2 1] [176°] (Barr), [188°] (Hentschel, *J pr* [2] 34, 427) S (95 pc alcohol) 76 at 21° (S), (88 p c alcohol) 5 8 (Rudneff, Z 1871, 202)

Formation -1 By the action of alkalis on di nitro phenyl citraconimide (Gottlieb, A 85, 17) — 2 By heating (1,2,4) chloro di nitro benzene with alcoholic ammonia (Clemm, J pr [2]1,145) —3 By heating $[4\ 2\ 1]$ C₆H₃(NO₂)₂(OMe) with NH3Aq at 100° (Salkowski, B 5, 872, 6, 139) -4 By heating (4,2,1) di-mitro phenol (3g) with ammonia $(10 \circ c)$ of $27 \circ c$ for 16 hours at 175° (Barr, B 21, 1542)

Properties - Light yellow prisms, v sl sol

boiling water Does not form salts

Reactions -1 Elimination of NH2 yields mdi nitro-benzene – 2 Conc KOHAq forms di-nitro phenol [114°] (Willgerodt, B 9, 979) – 3 Alcoholic KCy added slowly forms di nitro amido phenol [225°] (Lippmann a Fleissner, M7, 95).

Acetyl derivative C₂H₂(NO₂)₂(NHAc) [120°] Formed by nitration of acetanilide (Radneff, Z 1871, 202, Ladenburg, B 17, 148)
Tri-nitro annine C₂H₂(N₂)₂ te
C₄H₂(NO₂)₃(NH₂) [6 4 2 1] Picramide Mol w
228 [188°] Formed by the action of ammonia on (1,2,4,6)-chloro-tri nitro benzene (Pissan, A 92, 826) or on pictic ethers (Liebermann a Palm, B 8, 278) Formed also by dissolving p-bromo aniline in cooled HNO₃ (S G 1 5) (Hager, Yellow plates with blue shimmer B 18, 2578) (from alcohol) or monoclinic tables (from HOAc) Tin and HCl reduce it to tri-amido phenol (Hepp, A 215, 850) Nitrous ether does not attack it.

Dolling potash yields picric acid

Combinations — (O_cH_iN_iO_s)O_cH_c. Yellow
prisms, which separate from its solution in
benzene (Mertens, B. 11, 848)—B'C_iH_c—
B'O_sH_{ie}—B'O_sH_iNH₂. [124°] (Hepp, Bl [2] B'C₁₄H₁₀,—B'C₀H₁N 80, 4 A 215, 859)

References - Bromo, Chloro, and Iodo NITRO-ANILINE

NITRO ANILINE-SULPHONIC ACID NITRO-AMIDO BENZENE-SULPHONIC ACID

NITRO-ANISIC ACID v Methyl derivative of NITRO OXY BENZOIC ACID

NITRO-ANISOLE v Methyl ether of NITRO-PHENOL

NITRO ANTHRAQUINONE C,H,NO, ve $C_6H_4 < \stackrel{CO}{<_{CO}} > C_6H_3(NO_2)$ $\begin{bmatrix} 1 \\ 2 \end{bmatrix}$ 8 Mol [220°] Prepared by nitrating anthraquinone

dissolved in H2SO, by HNO, in the cold (Roemer, B 15, 1786, Liebermann, B 16, 54) plates (by sublimation) or prismatic needles (from HOAc), sol benzene, aniline, and chloro form, sl sol alcohol and ether On reduction and treatment with nitrous acid it yields erytho oxy anthraquinone

Nitro anthraquinone C₆H₄ CO C₆H₃NO₂

 $\begin{bmatrix} 1 \\ 2 \end{bmatrix}$ [230°] Formed by boiling anthraquinons for half an hour with HNO, (S G 15) (Bottger a Petersen, J pr [2] 6, 367, B 6, 20, A 166, 147) Formed also by nitration of di bromo anthracene (Claus a Hertel, B 14,978) Yellow needles (by sublimation), insol water, v sl sol ether and alcohol, m sol benzene and HOAc Yields alizarin on fusion with potash Conc H SO, (12 pts) at 200° forms ' imido oxy anthra quinone 'C sH16N O6, which sublimes in rose coloured needles

Di-nitro-anthraquinone C₁₄H₆N₂O₆ i c

[3 1/2]C₆H₃(NO₂) < CO > C₆H₃(NO₂) [1/2 6] Mol w
298 [above 300°] Prepared by allowing anthra quinone (10 g) dissolved in H2SO4 mixed with HNO3 (10 g of SG 148) to stand for several days It is also formed by nitrating o nitro an thraquinone (Roemer, B 16, 363) Yellow crystals (by sublimation), sol nitro benzene, sl sol xylene and HOAc, nearly insol alcohol and ether On reduction and treatment with nitrous acid it yields di oxy anthraquinone (anthrarufin) On heating with H_2SO_4 at 200° it yields four colouring matters, $C_3H_1N_2O_9$, $C_{28}H_{18}N_4O_7$, and $C_8H_1N_3O_0$

Di nitro anthraquinone C14H6N2O6 260°] Formed by boiling anthraquinone with a mixture of equal volumes of H2SO4 and HNO8 (SG 15), or by boiling anthracene with fuming nitric acid (Böttger a Petersen, A 160, 147, 166, Minute monoclinic, almost colourless, crystals, insol water, sl sol alcohol, v sl sol ether H_sSO₄ converts it at 200° into violet 'di imido di oxy-anthraquinone' C₁₄H_sN₂O₄

Di nitro-anthraquinone O₁₄H_sN₂O₅

Fritz

sche's Reagent [280°] Formed, together with anthraquinone, by heating anthracene with di lute nitric acid at 90° On crystallisation from alcohol it separates first (Fritzsche, N Petersb Acad Bull 22, 43, Z 1869, 114, cf Anderson, A 122, 302) Prepared by adding HNO₃ (30 g) to a solution of chrysene (50 g) containing an thracene in alcohol (5,000 c c), and heating on a water-bath The crystals of the chrysene compound (v smfra) which then separate are oxidised by CrO, in HOAc, which attacks the chrysene and leaves the di nitro anthraquinone (Schmidt, J pr [2] 9, 268)

Properties -Yellow needles (from boiling HOAc), v sl sol alcohol and ether Sublimes in colourless serrated plates Forms very characteristic compounds with aromatic hydrocarbons

H₂SO₄ at 200° forms O₁,H₂N₂O₄, a black powder.

Combinations — C₁₄H₂N₂O₄(PhCH CHPh):

orange red plates — C₁₄H₂N₂O₄(C₁₄H₁₀) violet monoclinic laminæ, obtained by dissolving dinitro anthraquinone (9 pts) and anthracene (10 pts) in crude xylene (100 pts)—With chrysene C₁₄H₆N₂O₆(C₁₈H₁₂) Slender red needles [294°], sl sol boiling HOAc

NITRO ANTHRAQUINONE CARBOXYLIC ACID C₁₁H₆O₂(NO₂) CO₂H [above 300°] Formed by nitration of anthraquinone carboxylic acid (Liebermann a Glock, B 17, 891) Small needles Dissolves in H₂SO, with a violet colour Small

(a) NITRO ANTHRAQUINONE SULPHONIC

 $\begin{array}{l} \textbf{ACID}' \textbf{C}_1, \textbf{H}, \textbf{NSO}, \textbf{1.e} \\ \textbf{C}_{\circ} \textbf{H}_{\bullet} < \begin{matrix} \textbf{CO} \\ \textbf{CO} \end{matrix} > \textbf{C}_{\circ} \textbf{H}_{2} (\textbf{NO}_{2}) (\textbf{SO}_{3} \textbf{H}) \begin{bmatrix} 1 \\ 6 \end{bmatrix} \textbf{2.3} \end{bmatrix}$ [255° Prepared by nitration of anthraquinone sulphonic acid with a mixture of HNO_3 (15) and H_2SO_4 , the (3) isomeric acid which is formed simultaneously remains dissolved whilst the α soid separates out (Claus, B 15, 1514, 17, 1276, Lifschutz, B 17, 899, cf

Liebermann, B 16, 55) Small white plates (from dilute HNO₃) or very fine silky needles (from hot water) Strong acid On fusion with KOH it gives alizarin

Salts -A'Na aq

long needles, sol hot water, nearly insol cold water and alcohol-A'K small needles —A'NH, jaq felted needles $-A'_2$ Ca microscopic needles, sl sol water -A'Ba needles

Chloride [194° uncor] Yellow concentric needles Nearly insol alcohol and ether

(β) Nitro - anthraquinone sulphonic acid C₁₄H₆O₂(NO₂)(SO₃H) [250° uncor] Crystal-line powder V sol water and alcohol Strong Crystalacid Formed as above Fusion with KOH gives no alizarin

Salts -K, Na, and NH, salts are extremely soluble — $A'_2Ba3_2^1aq$ needle white needles (Claus, B 15, 1516) needles —A'2Pb 2aq

Nitro anthraquinone (a)-di sulphonic Formed by nitration of the lead salt of anthraquinone-(a) di sulphonic acid with HNO, and H₂SO₄ (Claus a Schneider, B 16, 907) Yellow prisms Sol water, alcohol, and acetic acid, insol ether, chloroform, and ligroin

DI NITRO-ANTHRONE C14H₂N₂O₃ [116°] Formed as a by-product in the preparation of hydroanthracene-nitrite by the action of HNO. on an acetic acid solution of anthracene-dihydride (Liebermann a Landshoff, B 14, 472) Insol alkalıs, sol benzene

DI NITRO DIANTHRYL C₂₆H₁₆N₂O₄ ,C,H, ,C,H,∿ ONO. [8379]. V,H,

Formed by nitration of dianthryl in acetic acid solution (Gimbel, B 20, 2433) Yellow stellate needles V sol benzene and chloroform, sl sol. alcohol and acetic acid On reduction it gives di-amido-dianthryl [309°] By CrO, and scetic soid it is oxidised readily to anthraquinone. Bromine forms C. HieBr. [above 300°] (Sachse, B. 21, 2512)

NITRO-ARACHIC ACID C20H20(NO2)O2 [70°] Formed by mixing arachic acid with HNO, and H₂SO, (Tassinari, B 11, 2031) Sl sol cold alcohol, v sol ether

NITRO-ARBUTIN v ARBUTIN

TETRA-WITRO-AURINE $C_{10}H_{10}(NO_2)_4O_2$ [c 140°] Formed by nitration of aurine (Acker mann, B 17, 1625) Brownish-yellow micro V sol alcohol, nearly msol scopic needles water, benzene, chloroform, and ether solves in alkalis with a dark red colour

Salts -A"Ag, brown pp -A"Ba black

Ethyl ether A'Et, [c 105°], yellow crystals, v sol alcohol and benzene, insol water and carbonated alkalis

NITRO - AZO - compounds v Azo

Nitro-diazo- compounds v Di-azo- com POUNDS

NITRO-AZOXY- compounds v Azoxy- com

NITRO-BARBITURIC ACID C.H., N.O. .. CO NH CO CH NO Diliture acid Formed by the action of nitric acid on hydurilic acid and on barbituric acid (Schlieper, A 56, 23, Baeyer, A 127, 211, 130, 140) Colourless dimetric efflorescent prisms (containing 3aq), v sol hot water forming an intense yellow solution, m sol alcohol, insol ether Bromine and water at 100° decompose it into di bromo barbiturio acid and HNO. HIAq reduces it to amido barbit uric acid Its solution gives a white pp with ammonium salts

Salts -The salts are very stable, the acid not being separated by mineral acids—NH,H,A" crystalline pp,v sl sol cold water -NaH₂A"'2aq silky needles - KH₂A'' Ppd by adding HCl to a solution of the acid in potash - K₂HA'' yellow needles, insol alcohol and cone KOHAq Explodes when heated -BaH₂A"'Claq - Ca(H₂A'')₂4aq - Cu(H₂A''')₂6aq $-\operatorname{Fe}(\mathbf{H_{2}A'''})_{2}\operatorname{8aq}-\operatorname{Fe}(\mathbf{H_{2}A'''})_{3}\operatorname{9aq}-\operatorname{AgH_{2}A'''aq}\\-\operatorname{Ag,A'''}$

NITRO-BENZALDOXIM v Oxim of Nitro-BENZOIC ALDEHYDE

NITRO-BENZAMIDE v Amide of Nitro BENZOIC ACID

m-NITRO BENZAMIDINE

C_eH₄(NO₂) C(NH) NH₂. Formed from nitrobenzoic imido ethyl ether (Tafel a Enoch, B

 23, 1552) Colourless mass (from ether), v sol water—B'HCl [240°] Tables, v sol water m-NITROBENZAMIDOXIM C,H,N,O, t.e C,H,(NO,) C(NOH) NH₂. [174°] Formed from m ntro benzontrile and hydroxylamine (Schopff, B 18, 1063) Orange needles, v sol warm water ClCO_Et forms C_H_(NO) C(NH_2) NO CO_Et [158°] Acetic anhydride produces the azoxim $C^H(NO') \subset N > CWe [100e] - BHCI -$ B',H,PtCl,

Ethylether C,H,EtN,O, Prisms —B'HCl Bensyl ether C,H,(CH,Ph)N,O,. [58°] p Nitro-benzamidoxim

C.H.(NO2) C(NH2).NOH. [169°] Formed from p-nitro-benzonitrile and hydroxylamine (Weise, B 22, 2418) Yellow needles, sol acids and alkalis Reduces Fehling's solution and am monacal AgNO₂ M sol hot water and alco-

Can be distilled With Ac2O it yields hol $C_{\bullet}H_{\bullet}(NO_2)$ C < N O > CMe [144°], while aldehyde $C_*H_*(NO_*)$ $C \leqslant_{NH}^{NH} > CH CH^*$ CICO_Et produces C.H.(NO.) C(NH.) NO CO_Et [169°], which on heating yields the compound $C_{H_4}(NO_s) C \stackrel{N}{\leqslant} O CO [286^\circ]$ Sodium diazo benzene sulphonate produces the compound $C_H(NO) \subset NO \subset NH^3 \subset NH^3 \subset HNO^3$

(Stieglitz, B 22, 3157) COCl₂ reacts in benz-ene solution forming (C₆H₄(NO₂) C(NH₂) NO)₂CO [282°] —B'HCl [185°]

Ethyl ether C.H.(NO.) C(NH.) NOEt, [60°] Formed from the Na salt and Etl With nitrous acid it yields CoH4(NO2) C(O NO) NOEt [55°] -B'HCl

NITRO BENZENE C.H.NO. Mol w 123 [8°] (209°) at 745 mm (Bruhl, A 200, 188) S.G. 3º 1 2039 (B) S.V. 1219 (Lossen, A 254, 73), 1215 (Ramsay) $\mu_{\beta} = 15712$ R_{∞} = 52 64 Dispersive power Barbier a Roux, C R 108, 1249) Formed by intration of benzene (Mit scherlich, P 31, 625) The rate of nitration has been studied by Lothar Meyer (B 22, 18) small quantity by the action of ozonised air on a mixture of sulphuric acid and benzene (L Maquenne, Bl [2] 37, 298) Formed also by the action of ppd. Cu,O (1 mol) in the cold upon an aqueous solution of diazo benzene nitrite (1 mol), obtained by slowly adding a solution of 15 g NaNO₂ in 50 cc of water to a mixture of 9g of aniline, 20g HNO₃ (14), and 50 cc of water When the evolution of nitrogen has ceased the nitro benzene is distilled off with steam, the yield is 42 pc of the theoretical (Sandmeyer, B 20, 1494)

Preparation - A mixture of nitric acid (100 pts) and H,SO, (115 pts) is run into benz-The product is washed with alkali and

distalled

Properties -Oil, v sol alcohol and ether Not attacked by chlorine or bromine in the cold Reactions - 1 For bromination the presence of carriers (FeBr, or FeCl,) are necessary Thus nitrobenzene (10g) heated with FeBr, (3g) and bromine (43cc) in sealed tubes for 10 hours at 105° gives 65 p c of the theoretical amount of m-bromo nitro benzene When the same mixture is heated for 30 hours at 120° the product is tetra bromo nitro-benzene (Scheufelen, A 231, 158) Bromme at 250° forms C.H.Br. and a lttle C.HBr. (Kekulé, A 187, 169) — 2 Chlorine in presence of FeCl. forms m chloronitro benzene and (5,2,1) di chloro-nitro-benzene -3 Not attacked by boiling dilute potash or ammonia. Boiling alcoholic potash forms azoxybenzene—4 Readily reduced to aniline— 5 Chrome caychlorade forms a powder C₂H₃(NO₂)(CrO₂Cl)_p decomposed by water with reproduction of nitro benzene (Henderson a. Campbell, C J 57, 253, cf Etard, A Ch [5] 23, 272)—6 Exposed to sunlight in alcoholic solution it is reduced to amiline, aldehyde being formed (Ciamician a Silber, B 19, 2899, G. 16, 536).-7 Cone HClAq at 245° forms di-chloroaniline (Baumhauer, A Suppl 7, 204) -8 Reduced in alcoholic solution by sodium-amalgam

to azo benzene (Werigo, A 135, 176, Alexijeff, Bl [2] 1, 324)

o Di-nitro-benzene C.H.(NO2)2 [1 2] 168 [118°] S (alcohol) 38 at 248°, 33 at 78°. Formed in small quantity in the prepara tion of the m isomeride, and purified by succes sive crystallisations from alcohol and HOAc (Rinne a Zincke, B 7, 869, Körner, G 4, 354, Lobry, R T C 2, 239) Long colourless needles (from hot water) or monoclinic tables (from alco hol) (Bodewig, J 1884, 464) May be sublimed. Yields on reduction o nitro aniline [71°] and ophenylene diamine [99°]

m D1-nttro-benzene C₆H₄(NO₂)₂[1 3] (Reissert, B 23, 2243) (297° cor) (M (Reissert, B 23, 2243) (297° cor) (Meyer a Stadler, B 17, 2649 note) S (alcohol) 5 9 at 24 8° The chief product of the action of boiling fuming HNO, on benzene or nitrobenzene (Deville, A Ch [3] 3, 187, Muspratt a Hof-mann, A 57, 214) Formed also from (4,2,1)di nitro aniline by elimination of NH2 (Rudneff, Z 1871, 203) Prepared by adding benzene to a mixture of equal volumes of H2SO4 and fuming HNO, and heating until a sample of the oily layer solidifies on cooling. The product is poured into water, and the solid crystallised from alcohol (Körner, Beilstein a Kurbatoff, A 176,

Properties - Colourless flexible needles, v e sol boiling alcohol Detonates when projected into a red hot tube filled with nitrogen (Berthe lot, A Ch [6] 16, 24) A mixture with KClO,

100, A UN [0] 16, 24) A mixture with KClO₃ is a powerful explosive (rackarock)

Reactions—1 On reduction it yields mitro aniline [114°] and m phenylene diamine (Hofmann, Pr 11, 518)—2 Alcoholic KCy forms C₃H₃(NO) (OEt) CN (Lobry de Bruyn, R T C 2, 205)—3 Alkaline K₄FeCy₄ forms (4,2,1)—and (6,2,1) di nitro phenois (Hepp, B 13, 2547, A 215, 355)

p-D₁-nitro-benzene $C_6H_4(NO_2)_2[1 4]$ [172°] Deposited from the alcoholic mother liquor from which the m isomeride has crystallised (Körner) Flat monoclinic needles, sl sol cold alcohol May be sublimed Yields p-nitro aniline [146°] and p phenylene diamine [140°] on reduction Forms a sparingly soluble compound with naphthalene

t-Tri-nitro-benzene C₂H₃(NO₂), [1 2 4] [57 5°] SG 155 1 73 S (alcohol) 5 4 at 15 5°, S (benzene) 141 at 15 5° Formed by heating p di nitro benzene with a mixture of HNO, and

p di nitro benzene with a mixture of HNO₃ and H₂SO₄ (Hepp, A 215, 362, Lobry de Bruyn, R T C 9, 190) Yellow crystals Forms with aniline a compound C₆H₃(NO₂₎₃C₆H₃NH₂. [84°] Reactions — 1 NaOMe in HOMe forms C₆H₃(NO₂₎₂(OMe) [4 2 1] [88°] — 2 NaOEt forms C₆H₃(NO₂₎₂(OEt) [4 2 1] [86°] — 3 Boiling aqueous Na₂CO₃ forms (4,2,1) di nitro phenol [112°] 4 Alcoholic NH₄ forms di nitro aniline [175°]. s-Tri-nitro-benzene C₆H₃(NO₂₎₂ [1 3 5] [122°] Prepared by heating m di nitro benzene (40 g) with HNO₂ (120 g) and fuming H₂SO₂ (300 g)

with HNO. (120 g) and fuming H₂SO. (300 g) for one day at 80° and then for two days at 120°, the yield being 50 pc (Hepp, A 215,347, Claus, B 16, 1597) Trimetric plates, a bc = 954 1 788, sl sol. cold alcohol, y e sol benzene (forming a compound with CaHa) Not volatile with steam With annine it forms $C_cH_1(NO_2)_sNH_sPh$ crystallising from benzene in red plates [124°] With naphthalene it forms $C_6H_3(NO_2)_8C_{10}H_6$ [153°], and with dimethyl-

aniline C₆H₂(NO₂),NMe Ph [108°]

Reactions—1 Alkaline K,FeCy₆ oxidises it to pierie acid -2 NaOMe dissolved in HOMe forms, in the cold, $C_0H_1(NO_2)_2(OMe)$ [105°] (De Bruyn, R T C 9, 208) —8 Reduced by tin and HClAq to tri amido benzene

References -Bromo , Chloro , Chlorosodo-

and lopo nitro BENZENE

NITRO-BENZENE-AZO compounds v Azocompounds and DISAZO COMPOUNDS

NITRO-BENZENE-AZOXY- compounds v.

AZOXY- COMPOUNDS

DI NITRO-BENZENE TETRA-CARBOXYLIC ACID C₆(NO₂)₂(CO₂H)₄ [1 4 2 3 5 6] Di nitro-pyromellitic acid Formed by oxidising di nitrotri methyl benzoic acid with alkaline KMnO. (Nef, A 287, 19) Silky needles (from ether) Needles

i, A 287, 19) Dim, [130°] Nee
Ethyl ether Et, A' [130°] Nee
ENZENE PHOSPHONIC C₆H₄(NO₂)PO(OH)₂ Netrophosph [132°] S 98 at 22°, 92 at 98° Nitrophosphenylic acid Obtained by nitrating benzene phosphonic acid (Michaelis a Benziger, B 8, 1810, A 188, 275) Deliquescent crystals exploding above 200°—BaA" 2aq—
Ba(HA"), 2aq—CaA" | aq—PbA"—Ag.A"

m NITEO-BENZENE-SULPHINIC ACID

C₀H₄(NO₂)SO.H[1 3] [95°] Formed, together with nitrobenzene and N₂, by boiling the compound C₀H₄(NO₂) NH NH SO₂C₂H₄(NO₂) with baryta water Long silky needles

ether, sl sol alcohol

Salts - KA' small e sol prisms - AgA'. long silky needles, sl sol water -BaA'2 12aq yellowish prisms (Limpricht, B 20, 1240)

o Nitro-benzene sulphinic acid

 $C_e \hat{H}_4(NO_2) SO_2 H [1 4] [120^{\circ}]$ Formed in the same way as the preceding acid from the corresponding p-compound Plates Less soluble in ether than the m isomeride —BaA'2aq yellowish

prisms (Limpricht, B 20, 1241)
o-NITRO-BENZENE SULPHONIC C.H.(NO2)SO2H[12] Formed in small quantity in the nitration of benzene sulphonic soid (Limpricht, 4 177, 60) —NH, A' long needles -KA' sl sol water -BaA'2 aq v e sol water -PbA'2 3aq

Chloride C.H. (NO.) SOCI [67°]

Amide C₆H₄(NO₂)SO NH₂ [186°] Reduced by HI in HOAc it yields C.H. [198°] (Cleve, B 20, 1534)

m Nitro benzene sulphonic acid

C₆H₄(NO₂)(SO₃H) [1 3] Formed by sulphonating nitro-benzene, or by nitrating benzene sulphonic acid (Schmidt, A 120, 163, Meyer a Stuber, A 165, 164, Rose, Z 1871, 224, Limpricht, A 177, 60) Formed also by the action of ClSO₃H on nitro benzene in CS₂ (Armstrong, Z 1871, 821, Limpricht, B 18, 2175) Deliquescent Prisms — KA' S 1 7 4-4 A', an lamina -NH,A' Taming — N. 1.4. This — S. 1.4. This B (of CaA'₂) to at to —mgA'₂ aaq — ZulA'₂ oaq —
PbA'₂ 2aq S (of PbA'₂) 4 at 10°

Chloride C₂H₄(NO₂) SO₂Cl [61°]

Amide C₂H₄(NO₂) SO₂NH₂ [161°] Reduced

by HI and HOAc to C₂H₄(NO₂) [88°]

p.NITEO-BENZENE SULPHONIC ACID

C.H.(NO.)SO.H[1:4] Formed in small quantity | BENZAMIDOXIM.

in the nitration of benzoic acid (Limpricht) -NH₄A' Plates S 8 5 at 7° — KA' Prisms S 3 7 at 7° — BaA'₂3aq S (of BaA'₂) 4 6 at 6° — CaA'₂2aq — PbA₂2aq S (of PbA'₂) 11 8 at 5 5°. The solubilities of salts here given are the weights dissolved in 100 cc of the solution.]

Chloride $C_6H_4(NO_2)$ SO_2Cl Oil Amide $C_6H_4(NO_2)$ SO_2NH_2 [131] [131° (a) Nitro-benzene m-disulphonic acid

C₆H₃(NO₂)(SO₃H)₂. Formed, together with the (β) isomeride, by nitration of benzene m-disulphonic acid (Heinzelmann, A 188, 160, 190, 222) Slender deliquescent needles (containing 2aq) –(NH_a)₂A' flat prisms – K₂A'' – BaA''4aq. – BaA'' 5aq – BaA'' 6aq – Ba₂A'' (OH)₂ 15aq – PbA'' 4aq – Pb₂A''O 2jaq – Ag₂A'' Chloride C₃H₃(NO₂)(SO₂NH₂)₂ [96°] Amide C₃H₃(NO₂)(SO₂NH₂)₂ [242°].

(8) Nitro bengena endisminhania and

(β) Nitro benzene m-disulphonic acid

 $C_6H_3(NO_2)(SO_3H)_2$ [4 1 3] Formed as above. Very hygroscopic crystals Its salts are more soluble than those of the (α) isomeride $-(NH_4)_*A''$ -K₂A" aq (?) —BaA" 5aq —PbA" 4aq Chloride C₆H₂(NO₂)(SO₂Cl)₂ Oil

Nitro-benzene disulphonic acid C₆H₃(NO₂)(SO₃H)₂. Formed from nitro-amidobenzene disulphonic acid by the diazo- reaction (Limpricht, B 8, 289) -PbA" ag needles

Di nitro-benzene sulphonic acid $C_{g}H_{1}(SO_{3}H)(NO_{2})_{2}[1\ 2\ 4]$ [108°] Formed from $(C_nH_s(NO_s)_s)_sS_s$, and fuming HNO_s (Willgerodt a P Mohr, J pr [2] 34, 117) Very hygroscopic yellow prisms (containing 3aq), v sol water, sl sol ether, insol benzene Not attacked by

fuming HNO, at 200°

Reactions —1 Aniline forms, on boiling, C₆H₃(NO₂)₂(NPhH) [156°] -2 Boiling alcoholic ammonia forms C₆H₃(NO₂)₂(NH₂) [178°] -8 KHS forms, in the cold, C.H. (NO2)2SH-4 Rapidly decomposed by cold potash, becoming dı nıtro phenol [114°]

- NaA'aq — BaA'aq -

Salts — KA' — NaA'aq — :
CaA', 2aq — ZnA', 6aq — PbA', 3aq
Chloride C.H.(SO,Cl)(NO₂),
Amide C.H.(SO,NH₂)(NO₂),
Di-nitro-benzene sulphonic acid [102°] [1549]

C₆H₄(NO₂)₂SO₂H [8 2 1] Formed by warming Celling 2 2 1 Formed by warming nitro-benzene m-sulphonic acid with H.SO₄ (1 vol.) and HNO₂ (3 vols.) (Limpricht, B.9, 554, Sachse, A. 188, 143) Deliquescent crystals. NH₄A'—KA'1½aq—BaA', 3aq—PbA', 3aq—Chloride C₆H₃(NO₂), SO₂NH₄ [238°]

Amide C₆H₃(NO₂), SO₂NH₄ [238°]
Dimitro-bensene disalphonic acid

Di-nitro-benzene disulphonic acid $C_6H_2(NO_2)_2(SO_3H)_2$. Formed by boiling nitrobenzene m sulphonic acid with H_2SO_4 (1 vol) and fuming HNO, (6 vols) (Limpricht, B & Its chloride and Crystalline mass amide are crystalline and decompose without melting —K₂A" aq —Na₂A" 3aq —BaA" 2aq —CaA" aq —PbA" 3aq —CuA" 3aq

Tri-nitro-benzene sulphonic acid C.H. (NO.) SO.H [185°] Prepared by boiling chloro-tri nitro phenol (picryl chloride) with alcohol and dry NaHSO, (Willgerodt, J pr [2] 32, 117) Large crystals (containing 2aq), melting at 100° when hydrated Decomposed by alkalis in the cold into SO, and picric acid -NaA' 2ag

NITRO-BENZENYL-AMIDO-OXIM v Nitro-

NITRO-BENZIDINE v NITRO DI p-AMIDO-

[1420]. WITRO-BENZIL C, H, (NO2)O2 Formed by nitration of benzoin or benzil (Zinin, Suppl 8, 153, Hausmann, B 23, 531) Yellow crystals, sl sol alcohol

(a)-Dioxim O, H, N,O, [225°] Formed by heating nitrobenzil with hydroxylamine hydro chloride at 100°. Crystalline body, v. sl sol.

alcohol.

(8)-Droxem [185°] Formed by heating the (a)-isomeride with alcohol at 165° for several hours White needles, v sol alcohol Like the (a)-isomeride it is split up by conc HClAq at 100° into hydroxylamine and nitro benzil

Di-nitro-benzil C_1 , $H_s(NO_s)_2O_2$ [131°] (alcohol) 78 in the cold, 24 at 78° Form Formed. together with the following isomeride by boiling benzil with fuming HNO, (Zagumenny, J R 4,

278). Octahedra or moss like forms

Di-nitro-benzul [147°] S (alcohol) 34 in the cold, 19 at 78° Formed as above Plates Iso-di-nitro-benzil $C_{14}H_8(NO_2)Q_2$ [205°] (95 pc alcohol) 042 in the cold, 9 on 9 on boiling Formed by oxidation of (a)- or (γ) dintro-deoxybenzoin by CrO, in HOAc (Golubeff, J. R 13, 29, B 17, 581) Yellow needles o-NITRO-BENZOIC ACID C₆H₄(NO₂) CO₂H

[147 7°] (Reissert, B 23, 16 5° Formed in small [1 2] Mol w 167 8 61 at 165° 2244) quantity in the preparation of the m isomeride by nitration of benzoic acid (Griess, B 8, 526, A. 166, 129, L Liebermann, B 10, 862, Widnmann, A 193, 204) Obtained also by saponifying its nitrile Prepared by oxidising o nitro cinnamic acid with chromic acid mixture (Beilstein a. Kuhlberg, A 163, 134, Widnmann, B 8, 393) or, better, by oxidising o nitro toluene (Weith, B 7, 1058, Widnmann, A 193, 225, Noyes, B 16, 53, Monnet, Reverdin, a Nolting, B 12, 443) or o-nitro-benzyl chloride (Nolting, B 17, 385)

Properties - Small triclinic needles (from water), v sol alcohol and ether, v sl sol water Has a sweet taste. Very slightly volatile with

Salts.—BaA', 3aq Trıclım sol. water —CaA', 2aq needle AgA' Crystals, v sol hot water Triclinic crystals, v. needles -PbA'2aq -

Ethyl ether Eth' [30°] Triclinic crystals.

Ohloride C.H.(NO.) COCl Oil

Oyanide C.H.(NO.) CO CN [54°] Formed from the chloride and AgOy at 100° (Claisen a Shadwell, B 12, 351) White prisms

Anhydride (C₆H₄(NO₂) CO)₂O [135°]

Needles (Bischoff a Rach, B 17, 2789)

Amide C.H. (NO.) CONH. [176°] (Bischoff, A 239, 109) With KOH and bromine it yields C.H.(NO.)(CONHBr) converted by boiling potash into o-nitro-aniline (Hoogewerff a Van Dorp, R T C 8, 178)

Di-nitro anilide

C₆H₄(NO₂) CO NHC₆H₅(NO₂)₅. [178°] Formed by nitrating benzoyl-m-nitro-aniline (Schwartz,

B 10, 1708

Netrate C.H. (NO.) CN o-Nutro-bensonutrale Mol w 148 [110°] Obtained by heating the amide with P.O. at 100° (Hubner a Bartlein, B 10, 1718). Formed also by the action of hot cuprous potassium cyanide on o-nitro diazo-bensene chloride (Sandmeyer, B 18, 1494) and by treating the oxim of o-nitro-benzoic aldehyde

with Ac.O (Gabriel a Meyer, B 14, 2338) Needles, v sol water and alcohol

m-Nitro-bensoic acid C_eH₄(NO₂) CO₂H [1.3]. [141°]. S 25 at 10°, 10 at 100° (Mulder); 235 at 16 5° (Beilstein) Formed by nitration of benzoic soid (Mulder, A 34, 297, Gerland, A 91, 185, Hubner, A 222, 72) Formed also by boiling nitro-hippuric acid with HClAq (Bertagnini, A 78, 104, 79, 259) and by the oxida-tion of m-nitro toluene (Beilstein, A 132, 137, 155, 25, 163, 136) Obtained also by the action of hot cuprous potassium cyanide solution upon m nitro-diazo benzene chloride, and saponification of the crude nitrile, the yield being 72 pc (Sandmeyer, B 18,1494)

Properties - Colourless laminæ (from water), v e sol alcohol and ether May be sublimed Crystallises in three monoclinic modifications (Bodewig, J 1879, 677) Yields amido benzoic acid on reduction and azoxybenzoic acid on heating with alcoholic potash (Griess, A 131,92)

Salts - NH,HA'2 - NaA' 3aq colourless les - KA'aq Needles S 14 in the cold, tables —KA'aq 200 at 100° (Sokoloff, J 1864, 343) —MgA'. 7aq —CaA'₂2aq S 3 3 in the cold, 5 5 at 100° — Ca(OBz)A' 3aq (Salkowsky, B 10, 1258) — $\operatorname{SrA}'_{2}2\frac{1}{2}\operatorname{aq} - \operatorname{SrA}'_{2}4\operatorname{aq} - \operatorname{BaA}'_{2}4\operatorname{aq}$ S 38 in the cold, 5 3 at 100° (Sokoloff) S (of BaA'₂) 22 at 9° (Mills, C J 19, 363) —ZnA'₂5aq —ZnA'₂4aq S 16 in the cold 7 7 at 100° — CdA'₃4aq (Schiff, A 104, 326) —PbA'₂ — MnA'₂4aq —FeA'₂ —CuA'₂aq —AgA'

Methyl other MeA' [70°1 (279°)Prisms (Chancel, Compt Chim 1849, 179, A.

Ethyl ether EtA' [43°] (Tafel a Enoch, B 23, 1551) (296°) Monoclinic prisms Decomposed by bromine at 170°-200° into nitrobenzoic acid and ethylene bromide (Naumann, A 133, 202)

s-Tri-chloro-phenyl ether CaH2Cl2A'. [182°] Formed by nitrating the benzoyl de rivative of (6,4,2,1) tri chloro phenol (Daccomo, B 18, 1165)

Di bromo phenyl ether C.H.Br.A' v. vol 1 p 607

Nitro phenyl ethers v Nitro benzoyl derivatives of NITRO PHENOLS

Chloride C,H,(NO₂) COCl [34°] (184° at 50 mm), (275°-278°) Prisms (Cahours, A Ch [3] 23, 339, Hugh, B 7, 1267, Claisen a Thompson, B 12, 1942)

Cyanide C.H.(NO2) CO CN (231° at 145 mm) Formed from the chloride and AgCy (C.

Heavy oil

Anhydride (CaH4(NO)) CO)2O Solid (Gerhardt, A 87, 158)

Acetec-m netro-benzoec anhydride $C_sH_s(NO_s)$ CO OAc [45°] Formed from the Ag salt and AcCl (L Liebermann, B 10, 863, Beilstein, Bn 2, 786, Greene, Am 11, 414)

Benzoic-m nitro-benzoic anhydride C_sH₄(NO₂) CO OBz Crystalline (Gerhardt) Amide C.H. (NO2) CONH2 [142°] Needles (Field, A 55, 45, Chancel, Compt Chim 1849, 180, Beilstein, A 132, 137, Schiff, A 218, Its alcoholic solution mixed with 185) AgNO, and NaOH gives a gelatinous pp of O.H.(NO.) CO NHAg (Tafel a Enoch, B 23, 1550) With bromine and potash it gives m-nitro-aniline (Hoogewerff a Van Dorp, R. T. G. 8, 173) With m nitro benzoyl chloride it is converted into its m-nitro benzoyl derivative [195°] (W Schulze, A 251, 158)

Anslide C.H.(NO.) CONHPh [144]. Plates (Engler a Volkshausen, B 8, 34, Hubner, B 9, 774)

m-Nitro-anilide

C.H.(NO.) CO NHC.H.NO. [187°] Needles (from amyl alcohol) (McHugh, B 7, 1268) Dr nitro-anilids

 $C_bH_4(NO_2)CO\ NHO_bH_4(NO_2)$ [1 2 4] [165°] Formed by nitration of the benzoyl derivatives of o and p nitro-aniline (Schwartz, B 10, 1708

p To $luide C_0H_4(NO_1)$ CO NHC, H_4Me [162°]. Needles (from alcohol) (Hubner, A 210, 335)

Netro p-toluede

 $C_cH_4(NO_2)$ CO NH.C.H.Me NO₂ [1 4 2] [188 5°]. Yellow silky needles (from alcohol) Formed by nitrating the p toluide

MesidideC.H.(NO2) CO NHC.H.Me. [205°]

Netro messidede C₆H₄(NO₂) CO NHC₆H(NO₂)Me, [207°] Formed, together with the following, by intrating the messidide (Schack, B 10, 1711)

Di-nitro-mesidide

C₆H₄(NO₂) CO NHC₆M₆₁(NO₂)₂ [307°] Needles Nitrils C₆H₄(NO) CN [117°] Formed by nitrating benzontrile, or by dehydrating mitro benzoic amide (Beilstein a Kuhlberg, A 146, 336, Engler, Z [2] 4, 613, A 149, 297, Fricke, B 7, 1321) Formed also by the action of hot cuprous potassium cyanide solution upon mitro-diazo benzene chloride (Sandmeyer, B 18, 1494) Prepared by adding benzontrile (10 mols) to KNO₂(11 mols) dissolved in H₂SO₄below 25° (Schöpff, B 18, 1063) Needles (from water), sl sol water, v sol alcohol and ether

p Nitro benzoic acid $C_0H_1(NO_2)CO_2H$ [14] [238°] S 075 at 16° Formed by the action of fuming HNO, on toluene (Glenard a Bou dault, A 48, 344, G Fischer, A 127, 137, 130, 128, Beilstein a Wilbrand, A 126, 255, 128, 257), and by oxidising p nitro toluene with chromic acid (Beilstein a Geitner, A 139, 335, Korner, Z [2] 5, 636, Rosenstiehl, Z [2] 5, 701) Produced also by the oxidation of p nitro cinnamic acid, and, in small quantity, by the nitration of benzoic acid (Griess, B 8, 528, Ladenburg, B 8, 536) Obtained also by the action of a hot cuprous potassium cyanide solution upon p nitrodiazo-benzene chloride, and saponification of the crude nitrile thus got (Sandmeyer, B 18, 1492) Prepared by oxidising p nitro toluene (50 g) with CrO_3 (250 g) and H_2SO_4 (110 g) diluted with water (450 g) (Schlosser a Skraup, M 2, 519, of Michael a Norton, B 10, 580)

Properties —Yellowish lamins (from water) or needles (by sublimation), v sol alcohol and ether Less soluble in water than the m and c- isomerides Reduced by tin and HCl to pamido-benzoic acid, and by sodium amalgam to

p-azo-benzoic acid

Salts—NH₁A' 2aq efflorescent lamins—NaA' 3aq triclinic crystals (Bilfinger, A 135, 154)—KA' 2aq S 33 in the cold, 200 at 100° (Sokoloff, J 1864, 348)—BaA', 5aq monoclinic crystals (Bücking a Haushofer, A 193, 212) S 4 in the cold, 12 5 at 100°—BaA' (OBz) (Salkowsky, B 9, 24)—CaA', 3aq efflorescent tables S 3 in the cold, 8 3 at 100°—CaA', 9aq—CaA' (OBz) 3aq (Salkowski, B 10, 1258)—

SrA'(OBz) aq —ZnA', 2aq S (of ZnA',) -7 at 17° (Mills, C J 19, 363), 1 25 at 100° —PbA', Methylether MeA' [96°]

Ethylether EtA' [57°]

Chloride C.H.(NO.) COCI [75°] (c. 204° at 105 mm) Slender needles (from ligroin) (Gevekoht, A 221, 335)

Amide C_eH₄(NO₂) CONH₂ [198°] Needles (Beilstein a Reichenbach, A 132, 143) Treat ment with bromine and KOHAq converts it into p-nitro-aniline

Anilide C, H, (NO) CONHPh [204°] (Leo, K 3, 552)

Nttrile C₆H₄(NO₂) CN [147°] Formed from the amide and P₂O₅ (Engler, A 149, 298, Fricke, B 7, 1321), or by the action of hot cu prous potassium cyanide solution on p nitro diazo benzene chloride (Sandmeyer, B 18, 1492) Laminæ (from alcohol), v sol hot alcohol

Fourth and fifth nitro-benzoic acids have been described by Fittica (B 8, 252, 710, 741, 9, 788, 10, 481, J pr [2] 17, 188), but their existence has been contested by other chemists (Leo Liebermann, B 10, 1038, Widmann, B 10, 1159, Claus, B 13, 891)

(4,3,1) Di nitro-benzoic acid C,H₄N₂O₆ ie C₆H₅(NO) CO₂H [4 3 1] [161°] S 673 at 25° Prepared by heating p nitro benzoic acid with nitric and sulphuric acids in sealed tubes, and separated from the (4,2,1) isomeride, simultaneously formed, by the greater solubility of the latter in water (Claus a Halberstadt, B 13, S15) Colourless crystals Sol alcohol, ether, and hot water, sl sol cold water Very bitter taste Sublimes undecomposed

Salts — A'Ba 4aq white crystals — A'.Ca 3aq plates The potassium, sodium, and ammonium salts are easily soluble

Di-nitro-benzoic acid C₈H₃(NO)₂(CO₂H) [5 2 1] [177°] Formed, together with the (4,2,1) and (6,2,1) isomerides by boiling o nitro-benzoic acid with a mixture of fuming HNO₂ (1 pt) and H.SO₄ (1 pt) for 15 minutes (Griess, B 7, 1223) Needles or prisms, sl sol cold water, m sol hot water The di amido benzoic acid, obtained by reduction, yields p phenylene diamine on distillation—BaA' 4aq six sided plates, sl sol hot water

Di nitro-benzoic acid C₆H₄(NO),CO H[4 2 1] [1799] S 1849 at 25° Formed in the prepation of each of the two preceding acids (Gries, B 7, 1225, Claus a Halberstadt, B 13, 816, Hubner a Stromeyer, B 13, 461, A 222, 79) Obtained also by heating di-nitro toluene with fuming HNO₃ at 100° for a fortnight (Tiemann a Judson, B 3, 223) White needles or tables May be sublimed Tastes bitter On reduction with tin and HClAqit at once yields m phenylenednamine—BaA', 28aq m sol cold water—CaA', 2aq—MgA', 9aq

Di-nitro-benzone acid C_sH₁(NO_s)₂CO₂H [6 2 1] [202°] Formed, together with styphnic acid C_sH(NO_s)₂(OH)₂ and the (4,2,1)- and (5,2,1)-dinitro benzone acids, by heating o nitro-benzone acid with HNO_s and H₂SO₄ (Griess) Felted needles (from boiling water), v sol boiling water Tastes intensely bitter Split up on distillation into CO₂ and m-di-nitro-benzene On treatment with tin and HClAq it yields m-phenylene diamine—BaA'₂2aq v e sol cold water.

Di-nitro-benzoic acid CaHa(NO2)2CO2H [5 8 1] [204°]. S 19 at 100° Formed by nitration of benzoic acid or of m-nitro benzoic acid with a mixture of HNO₃ and H₂SO₄ (Cahours, A Oh [3] 25, 30, Voit, A 99, 100, Tiemann a Jud-son, B 3, 223, Muretoff, Z [2] 6, 641, Michler, A 175, 152) Obtained also by heating di-nitro-toluene [93°] with fuming HNO₃ at 150°, or by oxidising it with chromic acid mixture (Staedel, B 14, 902, A 217, 194, Hubner, A 222, 78), and in small quantity by the oxidation of 'β'-dinitro naphthalene with dilute HNO3 (SG 115) at 150° (Beilstein a Kurbatow, B 18, 355)

Preparation —1 By heating benzoic acid $(20\,\mathrm{g})$ with $\mathrm{H}_2\mathrm{SO}_4$ $(180\,\mathrm{g})$ and fuming HNO, $(50\,\mathrm{g})$ for 4 hours nearly to boiling (Hübner) — 2 By heating m-nitro benzoic acid $(100\,\mathrm{g})$ with fuming nitric acid (500 g) and H₂SO, (600 g) for

12 hours (H)

Properties -Thin tables (from dilute HNOs) or monoclinic crystals (Henniges, J 1882, 902 ▼ sl sol cold water, sl`sol dilute HNO,, v sol alcohol and HOAc Reduced by tin and HCl to di amido-benzoic acid, which yields m phenylenediamine on distillation with baryta

Salts -- NaA' -- KA' -- BaA' aq (Hubner) m sol hot water BaA'₂5aq (Muretoff)— CaA'₂aq — MgA'₂8aq — MnA'₂2aq — PbA'₂aq — AgA' needles (from hot water)

Ethylether EtA' [94°] (H), [91°] (B a

K) S (90 pc alcohol) 562 at 13°

Amide C₅H₃(NO₂), CONH₂ [183°] (Voit, A

99, 105), [177°] (M) Plates (from water)

Tri-nitro-benzoic acid C₅H₂(NO₃), CO H

[190°] Obtained by bear Obtained by heating tri nitro toluene with fuming HNO, for a fortnight at 100° (T a Trimetric crystals, abc = 8871 572(Friedlander, Z K 1, 623) May be sublimed -AgA' plates, sl sol water

References - Bromo , Chloro , and Iodo-,

NITROBENZOIC ACIDS

o NITRO-BENZOIC ALDEHYDE

C₆H₄(NO₂) CHO M M), [46°] (F a H) Mol w 151 [44°] (G a

Formation -1 In small quantity, together with the m-isomeride, by adding benzoic aldehyde to a mixture of HNO, and H.SO. (Rudolph, B 13, 810, of Fittica, B 10, 1630)—2 By treatment of its oxim with chronic acid mixture (Gabriel a Meyer, B 14, 829) -3 By oxidising o-nitro-cinnamic acid with dilute KMnO₄ (Friedlander a Henriques, B 14, 2801) -4 By adding NaNO, to a cold solution of o nitrocinnamic ether in fuming nitric acid (F a H) -5 In small quantity by the action of water on the compound of o nitro-toluene with CrO2Cl2 (Richter, B 19, 1062)

Preparation -50 grms of crude o nitroennamic acid are suspended in $2\frac{1}{2}$ litres of water, neutralised with Na2CO3 and filtered The clear solution is put into a large stoppered bottle, 1 litre of benzene added, and kept cold during the reaction by the addition of ice 1225 cc, of a 6 pc solution of KMnO, is added by degrees, shaking continuously, in order that the nitro-benzaldehyde, as it is formed, may be removed by the benzene from the action of the oxidising agent The emulsion which is produced is now treated with a warm solution of 150 grms of sodium sulphite and HCl added, which dissolves the MnO. The benzene layer,

which contains the whole of the nitrobenzaldehyde is removed, and the latter obtained by dis-tilling off the benzene The yield is 50 p c to 60 pc of the theoretical (Einhorn, B 17, 119)

Properties — Long yellow needles (from water), sl sol water, v sol alcohol and ether. May be distilled Volatile with steam NaHSO, it forms a compound crystallising in

plates

Reactions -1 On reduction with tin and HOAc it yields anthranil C.H. CONH, the lactam of o amido benzoic acid (Friedlander a Henriques, B 15, 2105, cf Rudolph, B 13, 310) Reduced by FeSO, and NH, to amido benzoic aldehyde (Friedlander, B 15, 2572, 17, 456)— Yields o nitro benzoic acid on oxidation with dilute aqueous KMnO, It also undergoes this oxidation when administered to dogs (Sieber a. Smirnoff, M 8, 88) -8 Conc NaOHAq con verts it into o nitro benzoic acid and o nitro-benzyl alcohol—4 NaOAc and Ac₂O yield o nitro cinnamic acid by Perkin's reaction -5 On warming with a dilute alcoholic solution of urea a compound CoH4(NO2) CH(NH CO NH2)2 $[200^{\circ}]$ is formed (Ludy, M 10, 295) When a few drops of $H_{s}SO_{4}$ are added to an alcoholic solution of o-nitro benzoic aldehyde and urea there is formed a different compound $C_{19}N_4H_2O_7$ [170°] —6 With dimethyl-aniline it forms nitro tetra-methyl di amido tri phenylmethane C_eH₄(NO₂) CH(C_eH₄NMe₂)₂ —7 Aceto-acetic ether (2 mols) and NH₃ form o nitro phenyl di methyl pyridine dihydride dicarboxylic ether [120°] and a compound $C_{19}H_{20}N_4O_5$ [189°], forming a salt B'HCl, converted by nitrous acid into an indifferent isomeride [192°] (Lepetit, B 20, 1838) -- 8 Boiling cone aqueous KCy forms o-azoxy benzoic acid -- 9 Aldehyde and a little baryta water forms $C_0H_0NO_1$ [120°], converted by further treatment with baryta water into $C_0H_4(NO_2)$ CH(OH) CH₂ CH₂OH [109°], and by NaOHAq into indigo (Baeyer a Drewson, B 15, 2861) -10 Acetone and NaOH forms o-nitrostyryl methyl ketone, which on warming with more alkalı yıelds ındıgo

Oxim C.H.(NO.) CH NOH o Nitro w-nitroso toluene [96°] Formed by the action of hydroxylamine on the aldehyde in alcoholic solution, or by treating (2,4,1) nitro amidophenyl acetic acid with nitrous acid (Gabriel a Meyer, B 14, 826, 15, 3057, 16, 520) needles (from hot water), v sol alcohol and ether Dissolves in alkalis Tastes sweet HClAq at 160° decomposes it into o nitro-benzoic acid and NH, Boiling with Ac.O and NaOAc forms the nitrile of o-nitro benzoic scid

Methyl derivative of the oxim

C₄H₄(NO₂) CH NOMe [58°]

Phenyl hydraside C₅H₄(NO₂) CH N₂HPh.

[158°] (P), [148°] (L) Formed by adding [158°] (P), [148°] (L) Formed by adding phenyl-hydrazine to an alcoholic solution of the base (Pickel, A 282, 282, Ludy, M 10, 814) Scarlet needles, sl sol hot water, forming a

dark blue solution in conc H,80,

m-Nitro-benzoic aldehyde C,H,(NO2) CHO [8 1] [58°] Obtained by dissolving benzoic aldehyde (1 vol) in a mixture of furning HNO. (1 vol) and H,SO, (10 vols) in the cold (Bertagnini, A. 79, 259, 86, 190; Lippmann a. Hawhozek, B 9, 146, Friedlander a Henriques, B 14, 2802, Ehrlich, B 15, 2010) Needles ; (from water), m sol hot water, v sol alcohol

Reactions -1. Chromic acid oxidises it to m nitro benzoic scid -2 Tin and HOAc reduce it to m-amido-benzoic aldehyde -3 Ammonia forms (C,H,(NO,)CH),N, which on heating with aqueous KOH forms tri-nitro-amarın C21H15N5O6 4 Ammonia and acetoacetic ether form C.H.(NO.) C.NH.Me (CO.Et). [65°] (Lepetit, B 20, 1338, 2397) -5 Sodium succinate and acetic anhydride form nitro phenyl paraconic acid C.H.(NO2) CH CH(CO2H) CH2 CO O (Salomon-

son, R T C 6, 1) -6 When its benzene solution is shaken with H_2SO_4 there is formed C_sH₄(NO_s) CHPh₂[90°], while toluene, by similar condensation, yields C_sH₄(NO_s) CH(C,H₁)₂ [85°] (Tschacher, B 21, 188) — 7 Phenyl acetonitrile and alcoholic NaOEt yields the nitrile of nitroa phenyl cinnamic acid (Frost, A 250, 156) -8 After administration to a dog it is excreted as m nitro hippuric acid (Sieber, M 8, 88)

Combinations — (C,H,NO,)NH,SO,H laq colourless prisms — (C,H,NO,)NaSO,H baq. yellowish crystalline scales (from hot water) — (C,H,NO,)NPhH2SO,H2 needles (Schiff, A 195, 301) — (C,H,NO₃),PH, powder, insol alcohol Formed from the aldehyde, PH,, and HCl (Messinger a Engels, B 21, 333)

Oxim C, H, (NO,) CH NOH [119°] Needles (from water) (Gabriel, B 15, 3060) PCl, yields m nitro benzonitrile (Gabriel, B 16,520)

Iso-oxim [118°] Formed by passing HCl into an ethereal solution of the oxim, and decomposing the hydrochloride by Na₂CO₂ Needles (from ether) Combines with phenyl cyanate in ethereal solution with formation of C_sH_s(NO₂) CH NO CONPhH [75°], which readily changes into an isomeride [105°] By treatment with NaOMe and MeI it is converted into a mixture of two isomeric methyl derivatives CaH, (NO) CH NOMe melting at 69° and at 117° (Goldschmidt a Ernst, B 23, 2170) MeI acting on its silver salt gives the methyl ether, melting NaOEt and benzyl chloride yield a benzyl ether [148°] Phenyl cyanate in ethereal solution yields C.H.(NO.) CH NO CO NHPh [105°], crystallising in yellow needles

Phenyl-hydraside C.H.(NO.) CH N.HPh [121°] (Pickel, A 232, 232, Ludy, M 10, 315) Orange tables Yields an acetyl derivative C₁₁H₁₀(NO₂)N₂Ac [170°] (Schroeder, B 17, 2097) Nitrous acid converts it into (C.H. (NO.) CH N NPh)2NOH, which crystal lises in needles, forming a deep blue pp in H2SO.

p Nitro-benzoic aldehyde

C.H.(NO.) CHO[4 1] [106°]

Formation —1 By boiling p-nitro-benzyl
chloride (10 pts) with Pb(NO.)2 (14 pts), water
(60 pts), and HNO. (S G 1 3) (Fischer a. Greiff,
B 13, 670) —2 By oxidising p-nitro-connamic
ether (Friedlander a. Henriques, B 14, 2803) or ap di nitro cinnamic ether (Friedlander a Maly,

A 229, 212, cf Baeyer, B 14, 2317)
Preparation —1 By adding KNO, to a cooled solution of p nitro cunnamic and, or its methyl or ethyl ether, in strong H_2SO_4 , the yield is 60 pc to 95 pc (Basler, B 16, 2714) -2 45 pts of chromyl chloride (OrO₂Ol₂) are slowly added to 20 pts. p nitro-toluene, dissolved in 80 to 100 pts of CS₂. After standing for two days,

the pp (C_sH₁(NO₂)CH₂,Cr₂O₁Cl₄) is separated, washed with CS, and treated with water The CS₂ is driven off with steam, and the product recrystallised from water, yield, 60 pc to 70 p.c. of the nitro toluene (Richter, B 19, 1060)

Properties - Long colourless prisms (from hot water), sl sol water and ether, m sol alcohol May be sublimed Volatile with steam. Forms with NaHSO, a compound crystallising

in plates

Reactions -1 Chromic acid mixture oxidises it to p nitro benzoic acid.—2 Aniline forms C.H.(NO.) CH NPh [93°] -3 Dimethylaniline condenses with it to p nitro tetra-methyl-di pamido - tri - phenyl - methane - 4 When administered to dogs it is excreted as p-nitro-hippuric acid. – 5 With p tolurans and conc HClAq it forms C₄H₄(NO₂) CH(C₄H₂Me NH₂)₂ [172°] (Bischler, B 20, 3302) –6 Ammonia and acetoacetic ether form the compound C₂H₄(NO₂) C₃NH₂Me₂(CO₂Et)₂ [118°-122°] — 7 Indoxyl with HClAq and HOAc forms the indogenide C₂H₄(CO₂CO) CCH C₂H₄NO₂,

crystallising in red needles [273°]

**Oxim O.H.(NO.)CH NOH [129°] Reddishyellow scales (Gabriel a Herzberg, B 16, 2000) Iso-oxim [175°] (Behrend, A 263, 349)
Bensyl ether of the iso-oxim

 $C_0H_4(NO_2)$ CH $<_0^{N(C_1H_1)}$. [118°] Formed by oxidising (β) benzyl p nitro benzyl hydroxylamine with K. FeCy, (Behrend a König, B 23, 2750) Needles (from alcohol), split up by hot HClAq into p nitro benzoic aldehyde and (β) benzyl-hydroxylamine

Phenyl hydrazide C₈H₄(NO₂)CH N₂HPh Red needles (Pickel, A 232, 232). Forms a red solution in conc H2SO4 (Lüdy, M.

10, 315)

NITROBENZOIC ANHYDRIDE v Anhydride of NITROBENZOIC ACID

m NITRO-BENZOIC IMIDO-ETHYL ETHER $C_bH_{10}N_1O_3$ te $C_bH_4(NO)$ C(NH) OEt Formed by treatment of $C_bH_4(NO_2)$ CONHAg with EtI, followed by ethereal HCl (Tafel a Enoch, B 23, 1550) Yellow oil —B'HCl White mass, v sol water and alcohol, converted by hot water into m-nitro benzoic ether -B'H₂C₂O₄

NITRO-BENZONITRILE v Nitrile of NITRO

BENZOIC ACID

o NITRO-BENZOPHENONE C13H9NO3 8.6. C_sH_s CO C_sH₄(NO₂) o-Nitro di phenyl ketone [105°] Formed by oxidation of o nitro-diphenyl methane with CrO, in acetic acid (Geigy Koenigs, B 18, 2403) Colourless crystals

m Nitro-benzophenone C,H, CO C,H, NO. [95°] Formed by the action of m nitro-benzoyl chloride upon benzene in presence of Al, Cle (Geigy a. Koenigs, B 18, 2401, cf Becker, B 15, 2090) Yellowish needles 2090)

p-Nitro-benzophenone CeH4(NO2) CO CeH [138°] Formed by oxidation of p nitro-diphenyl-methane with CrO₃ in acetic acid (Basler,

B 16, 2717) Small white plates or needles. Sol benzene, hot alcohol, and hot water, sl sol. cold water, cold alcohol, ligroin, and CS,

(a)-Di-nitro-benzophenone (C₂H₄(NO₂))₂CO₄ [190°] Formed, together with a larger quantity of the (β) -isomeride, by heating benzophenone with fuming HNO₂ at 60° (Prätorius, B 10, 1855, 11, 744, Staedel, A 194, 349, 218, 344) Formed also by oxidation of the corresponding di-nitro di-phenyl-methane [183°] by CrO, in HOAc (Staedel a Sauer, B 11, 1747) Long needles (from HOAc) Yields on reduction diamido benzophenone [172°]

(β)-Di-nitro-benzophenone C₁₂H₂N₂O₃ [149°] Formed as above Laminæ (from benzene or HOAc) Yields on reduction di amido benzophenone [165°]

Oxim (C,H, NO2),C NOH [207°], small

yellow needles (from hot alcohol).

Phenyl hydrazide (O₅H₄NO₂)₂C N₂HC₅H₅, [220°], red powder, sol. acetic acid, al sol. alcohol, insol water (Münchmeyer, B 20, 510)

(γ)-Di-nitro-bensophenone C₁,H₈N₂O, [190°] Formed by oxidation of the di nitro di phenylmethane [118°] Crystals Yields on reduction

di-amido-benzophenone [131°].

Tetra-nitro-benzophenone C₁₃H₆(NO₂)₄O Formed by oxidising tetra-nitro diphenyl-methane (Staedel, A 218, 341) Needles

from HOAc).

p-NITRO-BENZOYL-ACETIC ACID C.H.NO. C₆H₄(NO₂) CO CH₂.CO₂H Nitro phenyl methyl ketone carboxylic acid [135°] Formed by digesting p nitro phenyl propiolic ether with H₂SO₄ (85 p c) at 35° till it is completely soluble in aqueous NaOH (Perkin a Bellenot, B 17, 326, 18, 952, C J 49, 444) Needles, v solubles. alcohol and ether, sol water FeCl, colours its alcoholic or hot aqueous solution reddish brown On heating by itself or with dilute acids or alkalis it splits up into CO, and p nitro-acetophenone

Methyl ether MeA' [107°] Monoclinic crystals, v sol hot alcohol NaOMe forms yellow crystals of C₂H₄(NO₂) CO CHNa CO₂Me, a body from which benzyl chloride produces

a body from which body, Co₂Me [57°] C₆H₄(NO₂) CO CH(C,H₁) CO₂Me [57°] Monoclinic crystals, a b c = 358 1 1 238, B = 72° 22' alcoholic solution is coloured brownish violet by FeCl. Nitrous acid acting on its ethereal solution forms C₆H₄(NO₂) CO C(NOH) CO₂Et [220°] Yields C₆H₄(NO₂) CO CHNa CO₂Et, crystallising in orange needles, whence aqueous AgNO, forms an explosive amorphous Ag salt The sodium salt is converted by ethyl iodide into the ether C₆H₄(NO₂) CO CHEt CO₂Et [40°]

NITRO-BENZOYL-ACETOACETIC ETHER v.

ACETOACETIC ETHER

o-NITRO-BENZOYL-ACETONE

C₁₀H₂NO₄ s.s NO₂.O₆H₄ CO CH₂ CO CH₄ [55°]. Got by boiling o-nitro benzoyl aceto acetic ether with H.SO. (1 pt) and water (2 pts) for 4 hours (Gevekoht, A 221, 332) Crystallised from benzoline Insol. water, v sol alcohol and benzoline ether Gives with phenyl hydrazine a compound melting at 120°, crystallising from alcohol in slender needles, possibly nitro di phenyl methylpyrazole (Fischer a Bulow, B 18, 2136)

p-NITRO-BENZOYL-ANGELIC ETHER C.H.(NO.) CO CH(C.H.) CO.Et [46°] Formed by the action of allyl lodide upon the sodioderivative of p nitro-benzoyl-acetic ether (Per-

kın a. Bellinot, B. 18, 957) Colourless plates
(a)-DI-NITRO-BENZOYL-BENZOIC AC ACID O.H.(NO.).O. [240°] Formed from bensoyl

benzoic acid, HNO₃, and H₂SO₄ (Plaskuda, B. 7, 988). Plates —BaA', aq —CaA', 2aq

(β)-Di-nitro-benzoyl-benzoic acid

C_sH_s(NO₂) CO C_sH_s(NO₂) CO₂H [212°] Formed by boiling di-nitro phenyl-p tolyl ketone with CrO, and HOAc (Plaskuda a Zincke, B 7, 984). Plates (from hot water)

o - NITRO - BENZOYL - BENZYL - MALONIC ETHER $C_6H_4(NO_2) \odot C(CH_2Ph)(CO_2Et)_2$. [94°] Formed from sodium benzyl malonic ether and o-nitro benzoyl chloride, or from benzyl chloride and sodium o nitro benzoyl malonic ether (Bischoff a Siebert, A. 239, 103) Prisms (from dilute alcohol) V sol ether and hot alcohol, sl sol ligroin Gives no colour with FeCl, Alcoholic KOH produces benzyl malonic acid and o nitro benzoic acid Ammonia forms o-nitro-benzamide and benzyl-malonic ether

NITRO-BENZOYL CHLORIDE v Chloride of

NITRO-BENZOIC ACID

NITRO-BENZOYL CYANIDE v Cyanide of NITRO-BENZOIC ACID NITRO-BENZOYL-FORMIC ACID v NITRO-

PHENYL GLYOXYLIC ACID o-NITRO BENZOYL MALONIC ETHER

C₆H₄(NO₂) CO CH(CO₂Et)₂ [54°] The sodium-derivative C₆H₄(NO₂) CO CNa(CO₂Et)₂ is formed by the action of NaOEt on di-nitro di benzoylmalonic ether, or of o nitro benzoyl chloride (1 mol) on disodio malonic ether (1 mol) (Bischoff, B 16, 1044, 17, 2791, 22, 387) Needles or prisms (from alcohol) FeCl, colours its alcoholic solution dark red Bromine acting on its sodium derivative forms the bromo derivative C₆H₄(NO₂) CO CBr(CO₂Et)₂ [72°] On reduction by zinc-dust and HCl it yields (Py 1,3) di oxyquinoline (Py 2) carboxylic acid, and other bodies

o-Di-nitro-di-benzoyl-malonic ether

[93°] Colourless (C₂H₄(NO₂) CO)₂C(CO₂Et) tables or prisms Obtained by the action of onitro benzoyl chloride (2 mols) on di sodio malonic ether (1 mol) in alcoholic solution By treatment with sodium ethylate one of the nitro benzoyl groups is removed with formation of sodio nitro benzoyl malonic ether and nitro benzoic ether By alcoholic NH, both benzoyl groups are removed with production of malonic ether and nitro benzamide (2 mols) (Bischoff a. Rach, B 17, 2789)

m-NITRO BENZOYL PEROXIDE

(C_sH₄(NO₂) CO)₂O₂ Oil, ppd by adding water to a solution of benzoyl peroxide in fuming HNO, (Brodie, Pr 12, 655)

DI - p - NITRO - DI - BENZOYL - SUCCINIC ETHER

C₄H₄(NO₂) CO CH(CO₂Et) CH(CO₂Et) CO O₂H₄(NO₂) [180°] Formed by the action of iodine on an ethereal solution of the sodium derivative of p nitro-benzoyl acetic ether (Perkin a Bellenot, C J 49, 452, B 18, 953) Needles Forms an amorphous di-sodium derivative

O NITRO-BENZYL ALCOHOL C,H,NO, 16. C.H.(NO.) CH.OH [74°] Prepared by the action of aqueous NaOH on o nitrobenzoic aldehyde (Friedlander a Henriques, B 14, 2804, Gabriel a. Borgmann, B 16, 2065, Geigy a Koenigs, B 18, 2408) Yellow needles, sl sol water Yields on reduction by sinc and HCl o-amido-bensyl Chromic soid oxidises it to oalcohol [82°] nitro benzoic acid.

78 Nitro-benzyl alcohol C₆H₄(NO₂) CH₂OH (175°-180° at 3 mm) Formed by heating m-mitro-benzoic aldehyde with alcoholic potash,

and ppg by water (Grimaux, Bl [2] 8, 433)

Preparation —2 pts of m-intro benzaldehyde are mixed with a cooled solution of 1 pt of KOH in 6 pts of water After standing overnight the product is extracted with ether, the yield is nearly the theoretical (Becker, B 15, 2091)

Oil, decomposed by distillation under atmo-

spheric pressure

p Nitro-benzyl alcohol C.H. (NO.) CH.OH [92°] Formed by heating its acetyl derivative with aqueous NH, at 100° (Beilstein a Kuhlberg, Z [2] 3, 467, A 147, 343) Formed also, together with di nitro p-toluidine, by warming the p nitro benzyl ether of di nitro-o-cresol with alcoholic NH₃ (Staedel, A 217, 183)

Preparation —1 Finely powdered p-nitro-benzaldehyde (1 pt) is added to 5 or 6 pts of 15 p c aqueous NaOH, and allowed to stand for 12 hours, it is then diluted with a little water and extracted with ether, the yield is 80 pc to 90 pc of the theoretical -2 20 pts of p nitro benzyl acetate (obtained by nitration of benzyl acetate) in 40 pts of boiling alcohol is treated with 35 pts of 15 pc aqueous NaOH, quickly cooled and poured into 200 pts of iced water, and the pp collected, the yield is about 75 pc (Basler, B 16, 2715)

Properties - Yellowish needles Yields 1 nitro benzoic acid on oxidation Concentrated nitric acid converts it into the nitrate

C_sH₄(NO₂) CH₂ O NO₂ [71°] (Staedel, B 14, 90)

Acetyl derivative C_sH₄(NO₂) CH₂OAc

[78°] Formed by dropping henzyl acetate Formed by dropping benzyl acetate ming HNO, Pale vellow needles into fuming HNO,

O NITRO BENZYLAMINE C,H,N,O, C₆H₄(NO₂) CH₂NH₂ Formed by heating onitro benzyl phthalimide with HClAq at 200° (Gabriel, B 20, 2228) Liquid, v sol water—B'HCl Needles, v sol water—B'H,PtCl, 2aq

Formyl derivative CH, AcN2O2 Formed by heating the hydrochloride with dry sodium formate and formic acid (Gabriel a Jansen, B 23, 2813) Crystals Yields quinazoline dihydride on reduction by zinc and HCl Acetul derivative [99°] Needles Yields

on reduction C₆H₄(NH₂) CH₂NHAc [113 5°] Benzoyl derivative [112°] Ne Needles (from hot alcohol) Yields on reduction

C₆H₄(NH₂) CH₂NHBz [109°]

m Nitro-benzyl-amine C_sH₄(NO₂) CH₂NH₂. Formed by heating m nitro benzyl phthalimide with HClAq (Gabriel a Hendess, B 20, 2869) Formed also from m nitro benzyl chloride and alcoholic NH_s (Borgmann, C C 1885, 456) Needles -B'₂H₂PtCl_e plates

Acetyl derivative C₆H₄(NO₂) CH₂NHAc

[91°] Needles, sol hot water

p Nitro-benzyl amine C.H.(NO2) CH2NH2. Prepared from p-nitro benzyl chloride by treatment with potassium phthalimide and decom position of the p-mitro-benzyl phthalimide (Hafner, B 23, 337) Strongly alkaline oil, absorbing CO₂ from the air Converted by nitrous acid into p nitro benzyl alcohol CS₂ forms OS, forms C.H.(NO.) CH,NH CS NH, CH, C,H,NO. [1989]. -B'HCl plates, m sol. water — R'H.PtCl. BHNO, needles, sl sol water

Acetyl derivative C.H.(NO.) CH.NHAc. [183°] Needles, sol water Formed by heating the base with Ac,O and NaOAc, or by nitration of the acetyl derivative of benzylamine (Amsel a Hofmann, B 19, 1286)

Bensoyl derivative [156°] Needles D1-p-nitro-di-benzyl-amine C14H12N2O4 2.6. (C_eH₄(NO₂) CH₂)₂NH [93°] Obtained, together with the following isomeride and tri nitro-tribenzylamine, by heating nitro benzyl chloride with aqueous NH, at 100° (Strakosch, B 6, 1056) Yellow plates (from alcohol) —B'HCl [212°],— B'2H2PtCl

Di nitro-di-benzyl-amine 100℃ [above

Formed as above —B'HCl [173°]

Tri-o nitro-tri-benzyl-amine $(C_0H_4(NO_2)CH_2)_2N$ [157°] Formed almost exclusively by heating o nitro-benzyl chloride with aqueous NH. Long yellowish needles. Sol benzene, sl sol alcohol Its salts are decomposed by water (Lellmann a Stickel, B 19, 1605)

Tri p nitro-tri benzyl-amine

(C_sH₄(NO₂) CH₂)₃N [163°] Formed by heating -nitro benzyl chloride with aqueous NH, (Stra-Needles (from HOAc)

Tri nitro-benzyl-amine N(CH2.C8H4 NO2)3. [159°] Formed by nitration of tri benzyl amine with a mixture of conc HNO, and conc H2SO Colourless crystals Sol hot acetic acid, insol. alcohol and ether (Marquardt, B 19, 1030)

o NITRO-BENZYL-ANILINE

C₆H₄(NO₂) CH₂ NHC₆H, Prepared by heating 2 mols of aniline with 1 mol of o-nitro benzyl chloride in alcoholic solution for 2 hours on the It crystallises in two allotropic water bath forms, of which the unstable form changes into the stable by fusion or by long keeping The unstable form crystallises in reddish-yellow needles, abc = 8585111587, monoclinic $\beta = 87^{\circ} 42' 52''$, and melts at [44°] The stable form crystallises in glistening brown triclinic prisms, $a \ b \ c = 16704 \ 1^{\circ}, a = 117^{\circ}, \beta = 137^{\circ} \ 40'6'', \gamma = 69^{\circ} \ 38' \ 44''$, it melts at $[57^{\circ}]$ V sol alcohol, ether, and benzene, sparingly in petroleumether Reduced by tin and HCl to C18H10N2 [83°] -B'HCl 3aq white needles, basified by much water

Acetyl derivative CoH, (NO2) CH2 NPhAc.

[75°] (Paal a Krecke, B 23, 2637) Benzoyl derivative

[101°] $C_{\bullet}H_{\bullet}(NO_{\bullet})CH_{2}$ NPhBz Well formed crystals, sol alcohol, ether, and acetic acid. v sol chloroform, sl sol petroleum-ether By reduction with tin and HCl it is converted into C.H.(NH.) CH.NPhBz [115°] (Lellmann a. Stickel, B 19, 1605, 24, 718, Söderbaum a. Widman, B 23, 2198)

Formyl derivative C₄H₄(NO₂) CH₂ NC₇H₇ CHO [77°] Yellow monoclinic plates, a b c = 548 1 1085, $\beta = 69^{\circ}$ 7' Yields phenyl-quinazoline dihydride. on reduction (Paal a. Busch, B 22, 2683)

m-Nitro benzyl-aniline

C.H.(NO2)CH2NHC.H. [86°] From m-nitro-benzyl chloride and aniline (Borgmann, C C. 1885, 456) Orange-red needles —B'HCl plates.

Nitro-benzyl-aniline C.H. (NO.)CH, NHC.H. [68°]. Formed from p-nitro-benzyl chloride and aniline (Strakosch, B 6, 1062) Golden yellow needles, sol hot alcohol -B'HCl Plates

Di-nitro-di-benzyl-aniline

(C,H,(NO,) CH,),NC,H, [206°] Formed in small quantity as a by product of the action of o-nitro benzyl chloride upon aniline Greenishyellow needles Sparingly soluble in acetic acid (Lellmann a Stickel, B 19, 1608)

m Nitro benzyl-aniline CoH, (NO2) NH C7H, [107°] From m diazo nitro benzene m nitro benzyl anilide by heating with conc HCl at 100° (Meldola a Streatfeild, C J 51, 114)

The Nitrosamine is an oil

p-Nitro-benzyl-anılıne $C_8H_4(NO_2)$ NH C_7H_7 , r148°9 [143°] From p-diazo-nitro benzene p-nitro-benzyl-anilide by heating with cone HCl at 100° (Meldola a Streatfeld, C J 51, 113, Meldola a Salmon, C J 53, 779) Golden scales a Salmon, C J 53, 779)

C,H4(NO2) N(NO) C,H, Nitrosamine

[108°

Acetyl derivative [109°] Benzoyl derivative

C_eH₄(NO₂) NBz CH₂Ph [194°] Needles

p-Nitro-di-benzyl-aniline $C_{e}H_{4}(NO_{2}) N(CH_{1}C_{6}H_{5})_{2}$ [130°] Formed by nitration of di benzyl aniline dissolved in acetic Yellow needles Sol hot alcohol and acetic acid, sl sol cold alcohol, v sol ether and benzene (Matzudaira, B 20, 1613)

NITRO-BENZYL-BENZENE v

PHENYL METHANE

Di-m nitro di benzyl-benzene C20H16N2O, i e C₆H₄(CH₂ C₆H₄NO₂)₂ [165°] Formed by the action of H₂SO, on a mixture of m nitro diphenyl methane and m-nitro benzyl alcohol (Becker, B 15, 2091)

Di-p nitro di-benzyl-benzene

 $C_6H_4(\overline{NO}_2)$ CH_2 C_6H_4 CH_2 $C_6H_4(\overline{NO}_2)$ Formed as a by product in the preparation of p-nitro-di phenyl methane by the action of H_2SO , on a mixture of p nitro benzyl alcohol and benzene (Basler, B 16, 2716) Small white concentric needles Sol benzene and hot acetic acid, v sl sol other solvents

m-NITRO-BENZYL BROMIDE C.H.Br NO. t.e. C₆H₄(NO₂) CH₂Br [58°] Formed by heating m-nitro toluene with bromine at 130°

(Wachendorff, A 185, 266)

p-Nitro-benzyl bromide [100°] from p-nitro toluene and Br (W) Formed Needles p-NITRO-BENZYL-CARBAMIC ETHER

C.H.(NO2) CH2 NH CO2Et [1179] from p-nitro benzylamine and ClCO2Et (Hafner, B 23, 840) Silky needles, v sol ether

837, Abelli, G 13, 97, Nölting, B 17, 385, Kumpf (A 224, 100) Formed also by treating o-nitro benzyl alcohol with PCl, in the cold (Gabriel a Borgmann, B 16, 2066, Geigy a Königs, B 18, 2401) Thick crystals Reduced by SnCl₂ to o-'benzylene imide' C,H,N, an amorphous base (Lellmann a Stickel, B 19, 1611) Anilme yields oily C.H.(NO.) CH_NHPh reduced by zinc-dust in HOAc to the amidocompound C.H.(NH,) CH,NHPh [82°] (Söderbaum a Widman, B 28, 2198)

m-Mitro benzyl-chloride C.H.(NO.) CH.Cl. [47°]. (c. 178° at 35 mm). Long yellow needles

V sol alcohol, ether, and benzene Formed by the action of PCl, on the alcohol (Gabriel a. Borgmann, B 16, 2064)
p-Nitro-bensyl chloride

[4 1] $C_sH_1(NO_s)$ CH_sCl [71°] Formed by treating benzyl chloride with HNO_s (S G 1 48) at -10° (Elbs a Bauer, J pr [2] 34, 343, cf Beilstein a Gettner, A 139, 337, Strakosch, B 6, 1056, Grimaux, Bl [2] 8, 433) Formed also by passing chlorine into p nitro toluene at 190° (Wachen

dorff, B 8, 1101, A 185, 271) Crystals
Reactions -1 Ammonium sulphide gives p-nitro benzyl mercaptan (Strakosch, B 5,697) Alcoholic potash gives an azo derivative of di nitro stilbene -3 An alkaline solution of SnO forms p dinitro dibenzyl (W Roser, A 238, 363) -4 Chromic acid mixture oxidises it to p nitro benzoic acid -5 A solution of SnCl, in HClAq reduces it to p 'benzylene imide' C,H,N, an amorphous base (L a S

NITRO BENZYL CYANIDE v Nitrile of

NITRO PHENYL ACETIC ACID

o - NITRO - BENZYL - ETHYL - MALONIC ETHER C_{1e}H₂₁NO_e i e C_eH₄(NO_e) CH₂ CEt(CO_eEt)₂ Formed from ethyl

malonic ether, NaOEt, ando nitro benzylchloride (Lellmann a Schleich, B 20, 440) Reduced by zinc and HOAc to C, H, NO. [1149]

p Nitro benzyl ethyl-malonic ether [52°]

Formed in like manner Needles o NITRO-BENZYL ETHYL OXIDE

C₆H₄(NO₂) O C₂H₅ Formed by heating o-nitro benzyl chloride with alcohol in a boiling brine bath (Errera, G 18, 232) Oil

m Nitro-benzyl ethyl oxide Prepared by heating m nitro benzyl chloride with alcoholic potash (E) Oil, solidifying in a freezing mix-

p Nitro benzyl ethyl oxide [24°] Prepared by heating p nitro benzyl chloride with alcohol (È) Trimetric crystals

NITRO BENZYLIDENE ACETONE v NITRO-STYRYL METHYL KETONE

NITRO BENZYLIDENE ACETONAMINE v. **ACETONAMINE**

m DI - NITRO - DI BENZYLIDENE - DI -AMIDO DIPHENYL

C₆H₄(NO₂) CH N C₆H₄ C₆H₄ N CH C₆H₄(NO₂) Formed by heating op di amido diphenyl with m-nitro benzoic aldehyde and alcohol at 100° (Reuland, B 22, 3011) Yellow crystalline powder, m sol alcohol The isomeric compound from p nitro benzoic aldehyde and op di amido diphenyl melts at 208°, while that from di pamido-diphenyl and m nitro benzoic aldehyde melts at 234° (Schiff a Vanni, A 258, 375)
m NITRO-BENZYLIDENE ANILINE

 $C_{13}H_{10}N_2O_3$ se [3 1] $C_6H_4(NO_2)$ CH NPh Formed from m-nitro-benzoic aldehyde and anılıne (Lazorenko, J 1870, 760) Needles

p-Nitro-benzylidene aniline

[93°] [4 1]C,H,(NO2) CH NPh Formed heating aniline with p nitro benzoic aldehyde at 100° (Fischer, B 14, 2524)

Di-m-nitro-benzylidene-aniline

[3 1]C.H.(NO.) CH N C.H.(NO.) [1 3] [158]. Formed by warming the alcoholic solution of m nitro-benzoic aldehyde with m nitro aniline (Hantzsch, B 23, 2775).

m-NITRO-BENZYLIDENE BROWIDE [102°] C_H_(NO_) CHBr_[1.8] Formed heating m-nitro toluene (1 mol) with bromine (2 mols) at 140° (Wachendorff, A 185, 278) Minute needles (from alcohol)

p-Nitro-bensylidene bromide

 $\mathbf{C_0H_4(NO_2)\ CHBr_2[1\ 4]}$ [82°] Formed by heat ing p ntro toluene (1 mol) with bromine (2 mols) at 140° (W) Needles or rectangular plates (from alcohol) By heating with aniline it yields p rosaniline (Zimmermann a Muller, B 17, 2936)

m-NITRO BENZYLIDENE CHLORIDE

 $\mathbf{C_{sH_{s}}(NO_{s})}$ CHCl [65°] Formed from m nitro benzone aldehyde and PCl, (Widmann, B 13, 676, Erlich, B 15, 2010) Thin monoclinic plates or needles (from alcohol), v sol ether

p-Nitro-benzylidene chloride

 $C_bH_s(NO_2)$ CHCl₂ [46°] Formed from p nitro benzoic aldehyde and PCl₃ (Zimmermann a Muller, B 17, 2937, 18, 997), and by nitration of benzylidene chloride (Hubner a Beute, B 6, 803) Prisms (from alcohol) Yields p-rosaniline on heating with aniline

o NITRO-BENZYLIDENE HYDRAZINE

(C₆H₄(NO₂) CH),N₂ [181°] Formed from o nitrobenzoic aldehyde and hydrazine salts (Curtius a Jay, J pr [2] 39, 43) Yellow needles

p-NITRO-BENZYLIDENE INDOXYL v Indogenide of p Nitro Benzoic Aldehyde

o-NITRO BENZYLIDENE MALONIC ACID C₁₀H₁NO₆ te [2 1]C₆H₄(NO₂) CH C(CO₂H)₂. [161°] Formed by heating o nitro benzoic aldehyde with malonic acid and HOAc at 60° (Stuart, C J 47, 158, 49, 365) Needles (from water), ▼ sol. ether, ▼ e. sol ether, sl sol CHCl₃ With HBr it yields a yellow compound melting at 227° Boiling water decomposes it slowly, forming o nitro benzoic aldehyde, malonic acid, and a little o nitro cinnamic acid — BaA" 21 aq feathery tufts, converted by warm water into insoluble BaA"aq —Ag A"

Ethyl ether Et.A" [53°]

m-Nitro-benzylidene malonic acid

[3 1] $C_0H_4(NO_2)$ CH $C(CO_2H)_2$ [205°] Formed from m nitro benzoio aldehyde, malonic acid, and HOAc (Stuart, C J 47, 155, 49, 361) Crystals, sl sol cold water and ether Partially decomposed by hot water into m-nitro benzoic aldehyde and malonic acid Split up on fusion into CO₂ and m-nitro-cinnamic acid [196°] HBr forms C₂H₄(NO₂) CHBr CH(CO₂H)₂. Bromine combines with it, yielding the dibromide C.H.(NO.) CHBr CBr(CO.H). Ethylether Et.A" [7

p-Nitro-bensylidene-malonic acid

C.H. (NO.) CH C(CO.H). [227°] Formed from p-ntro-benzoic aldehyde, malonic acid, and HOAc at 60° (Stuart, O. J. 43, 408) Formed also, together with a small quantity of the orthoacid from benzylidene malonic ether by nitration and saponification (Stuart, C. J 47, 155) Crystals, split up on fusion into CO, and p nitrocinnamic acid Decomposed by hot water into p nitro-benzoic aldehyde and malonic and Bromine forms C₂H₄(NO₂) CHBr CBr(CO₂H)₂ which gives off HBr at 100°, leaving a residue Ultime green in the state of th

m - NITRO - BENZYLIDENE DI . METHYL DISULPHONE C.H., NS,O, 2 e

[1 8]C,H,(NO,) CH(SO,CH,),. [179°]

by oxidising m-nitro benzylidene di thio di-gly-collie acid (Bongartz, B 21, 487) Slender needles (from dilute HOAc)

p-Nitro-bensylidene di-methyl disniphone [14]C₆H₄(NO₂) CH(SO₂CH₃)₂. [248°] Formed by oxidising p-nitro benzylidene di-thio di glycollic acid with KMnO₄ (B) Yellowish needles (from hot water)

NITRO-BENZYLIDENE PHTHALIDE

C₁₅H₉NO₄ t e C₆H₄CC(NO₂) C₆H₅

Preparation -10 pts of crude di nitrobenzyl phthalide are dissolved in 20 pts of hot alcohol, diluted with 10 pts of hot water, and heated for half an hour on the water bath, the yield is 46 pc of theoretical, but when pure di nitro compound is used, nearly 100 pe (Gabriel, B 18, 1251, 3471)

Properties -Glistening crystals Split up on dry distillation into phenyl cyanate and phthalic anhydride Alcoholic NaOH converts it into the salt C13H,NO,Na, 21 aq which crystal lises in colourless prisms and is decomposed by acids into ω nitro toluene C_0H_0 CH $_0(NO_2)$ and phthalic anhydride Reduced by HI and P to 180benzylidene phthalide C.H. CPh

[91°] and a compound C₁₅H₁₁NO₂ [257°] whence KOH and MeI yield two isomeric bodies $C_{16}H_{13}NO_2$ melting at 237° and 121° (Gabriel, B

NITRO-BENZYLIDENE-PHTHALIMIDINE

 $C_{13}H_{10}N_2O_3$ is C_0H_{\bullet} C_0 NH

Phthalimidyl nitro benzyl Formed together with oxy-nitro benzyl-phthalimidine by leading N₂O₃ or N₂O₄ into a benzene solution of benzalphthalimidine or of deoxybenzoin-o-carboxylamide C.H. (CO NH2) CO CH2 C.H. (Gabriel, B. 18, 2439)

Nitro-bensylidene-phthalimidic acid C₁₃H₁₂N₂O₄ 26 C₆H₄(CO₂H) C(NH₂) C(NO₂) C₆H₄ [145°-150°] Formed by dissolving nitro-benzylidene phthalimidine in hot dilute NaOH and precipitating with an acid (Gabriel, B 18, 2440) Acetyl chloride reconverts it into the anhydride Nitrous acid passed into the solution in benzene converts it into nitro-benzylidene phthalide

Salts -A'Ag microcrystalline powder -A'2Ba 7aq long yellow needles or short prisms

Ethyl ether A'Et [155°], yellow crystals. Nitro-iso benzylidene-phthalimidine (Py 1 4.2)-NITEO-OXY PHENYL ISOQUINOLINE

NITRO-BENZYLIDENE-DI-THIO-DI-GLY-COLLIC ACID $C_{11}H_{11}NS O_8$ s e $C_eH_4(NO_2)$ CH(S $CH_2CO_2H)_2$ The o , m-, and

p-varieties of this acid are formed by the action of thioglycollic scid on the three nitro-benzois aldehydes (Bongartz, B 21, 479)

o-Acid [123°] m-Acid [180°] Needles (from HOAc) Needles (from dil HOAc). p-Acid [162°] Needles (from dil HOAc) o-NITRO-BENZYLIDENE-DI-UREA

C.H. N.O. se. C.H.(NO.) CH(NH CO NH.). [200°] Formed by warming an alcoholic solu-tion of ures with o-nitro-benzoic aldehyde (Schiff,

A. 251, 186, Ludy, M 10, 804) Needles (containing aq), sl sol water and alcohol

o-MITRO-BENZYL IODIDE C.H.(NO2) CH2I [75°] Formed from o-nitro benzyl chloride, KI, and alcohol (Kumpf, A 224, 103) Plates p Nitro-benzyliodide C, H, (NO2) CH, I [127°]

Formed in like manner Needles

p-NITRO-BENZYL-MALONIC ACID C.H.(NO₂) CH₂ CH(CO₂H)₂ Formed by saponification of the ether which is obtained in small quantity, together with di nitro di benzylmalonic ether, by the action of p nitro benzyl chloride upon sodio malonic ether (Lellmann a Schleich, B 20, 434) Yellow powder Carbonises at 240° without melting CaA" and

BaA" yellow pps Ethyl ether Et2A" [63°], yellowish

prisms, sol ordinary solvents

Di o nitro-di benzyl malonic ether $(C_0H_1(NO_2) CH_2)_2 C(CO_2Et)_2 [97]$ Obtained by the action of o nitro benzyl chloride upon

sodio-malonic ether Yellow crystals alcohol and ether (Lellmann a Schleich, B 20,

 $\mathbf{D}_1 p$ nitro di benzyl malonic ether

 $(C_0H_4(NO_2)CH_2)_2$ $C(CO_1Et)_2$ [170°] Formed by the action of p mitro benzyl chloride upon sodio malonic ether Colourless silky needles acetic acid, sl sol alcohol, and chloroform

p-NITRO BENZYL MERCAPTAN C,H,NSO₂ te C₆H₄(NO₂) CH₂SH [140°] Formed from Formed from p-nitro-benzyl chloride and alcoholic ammonium sulphide (Strakosch, B 5, 698) Laminæ

TRI-NITRO-BENZYL-MESITYLENE

C₁₆H₁₅(NO₂), [185°] Formed by nitration of benzyl-mesitylene at 0° (Louise, A Ch [6] 6, Prisms (from alcohol chloroform)

TRI-NITRO-BENZYL METHYL KETONE C_eH₂(NO₂)₃CH₂CO CH₃ [89°] Obtained by boiling tri nitro phenyl acetoacetic ether (10 g) dissolved in HOAc (100g) with H_2SO_4 (20g) and water (30g) for 8 hours (Dittrich, B 23, 2723) Long yellowish white needles, sol alkalis

Phenyl hydrazide C₁₅H₁₃N₁O₆ [125°] NITRO p-BENZYL-PHENOL C₁₅H₁₁NO₅ ie benzyl phenol and HNO₃ (S G 14) Volatile with steam — KA' brick-re (Rennia C 7 4) brick-red needles

(Rennie, C J 41, 221)

Di nitro p benzyl-phenol Ph CH₂ C₆H₂(NO₂) OH [1 3 5? 4] [8**8°**] the above, HOAc, and HNO, Formed also by the action of HNO₃ on p benzyl phenol sulphonic acid (Rennie, C J 49, 408) Oxidised by CrO₃ it gives benzoic acid —KA', orange needles— BaA

Di-nitro o benzyl phenol [82°] Obtained by warming o-benzyl phenol sulphonic acid with

dilute HNO₃ (Rennie) — KA'aq — BaA'₂
Tri - nitro - benzyl phenol C₁₃H₃(NO₂)₃OH [148°] Got by dissolving potassic benzyl-phenol sulphonic acid in HNO₂ (S G 1 4) and evaporating (Rennie, C J 41, 36, 223) Silky pale yellow Yields p nitro-benzoic acid on oxidaneedles

tion with chromic acid mixture —C₁₈H_s(NO₂),OK NITRO - p - BENZYL - PHENOL SULPHONIC ACID *C,H, C,H2(OH)(NO2)SO2H -KA' Formed by action of HNO, (S G 1 2) and potassic benzylphenol sulphonate (Rennie, C J 41, 85)

Nitro - o - benzyl - phenol sulphonic soid Formed in like manner — KA · yellow scales

DI-NITRO BENZYL PHTHALIDEC, H., N.O. $C(NO_2) CH(NO_2) C_0H_0$

C,H [113°].

Formed by passing nitrous acid gas into a solution of benzylidene phthalide in benzene (Gabriel, **B** 18, 1251) Colourless crystals Readily converted into nitro-benzylidene phthalide (q v) o-NITRO-BENZYL-PHTHÂLIMIDE

 $C_6H_4 < \stackrel{CO}{<} N CH_2 C_6H_4(NO_2)$ [1 2] [2197].

Formed from potassium phthalimide and o nitrobenzyl chloride at 100°-130° (Gabriel, B 20, 2227) Prisms

m Nitro benzyl phthalimide [155°] Formed

in like manner Needles

p Nitro benzyl-phthalimide [175°] (S), [172°] (Hafner, C C 1889, 671) Prisms (from HOAc) (Salkowski B 22, 2142

p NITRO BENZYL-PIPERIDEÏN

C₆H₄(NO₂) CH₂ NC₅H₆ [35°-40°] Formed by dissolving its polymeride in HClAq and ppg by ammonia (Lellmann a Schwaderer, B 22, 1333) Readily polymerises to (C, H, (NO2) CH, NC3H8)2 [120 5°], which is also obtained by treating dipiperide \ddot{i} n with p nitro benzyl chloride and NaOHAg

NITRO BENZYL-PIPERIDINE

C₆H₄(NO₂) CH₂NC₅H₁₀ The o, m-, and pisomerides are formed by the action of o, m and p-nitro benzyl chloride on piperidine in hot alcoholic solution (Lellmann a Pekrun, A 259, 40)

o Isomeride Oil Reduced by SnCl, to oamido benzyl piperidine [82 5°] - B'HCl -

Oil Reduced by SnCl, to m m Isomeride amido benzyl piperidine [112°] —B'HCl

B'HCl —B',H,PtCl p Isomeride p Isomeride [34°] B'HCl —B', NITRO - BENZYL QUINOLINE TETRA HYDRIDE C.H. (NO) CH2NC.H10 The three isomerides are formed by heating o, m, and pnitro benzyl chloride (1 mol) with quinoline tetrahydride (2 mols) in hot alcoholic solution (Lellmann a Pekrun, A 259, 50)
o Isomeride [111°] Brownish red tables —
B'₂H,PtCl₆ yellow amorphous pp

m Isomeride [99°] Red prisms, reduced by SnCl₂ to m amido benzyl-quinoline tetrahydride [82°]

p Iso B'₂H₂PtCl. Isomeride [102°] Red prisms -

NITRO BENZYL SELENOCYANIDE

 $C_8H_6N_2SeO_2$ is $C_6H_4(NO_2)$ CH_2SeCN [122 5°] Formed by nitration of benzyl selenocyanide at -4° (C L Jackson B 8, 321, A 179, 16) Needles (from alcohol)

O NITRO BENZYL SULPHIDE

[124°] Formed, together $(C_6H_4(NO_2)CH_2)_2S$ with a little of the disulphide, by passing NH, and H.S into an alcoholic solution of o nitrobenzyl chloride (Jahoda, M 10, 880) White plates Yields on oxidation by HNO, the sulphoxide (C.H.(NO.) CH.) SO [163°] and the sulphone $(C_{b}H_{4}(NO_{2})CH_{2})_{2}SO_{2}[200^{\circ}]$.

o Nitro-benzyl disulphide (C.H.(NO.) CH.).28. [47°] Formed as above (J) p-Nitro-benzyl disulphide [89°] Yellow Yellow

crystals (Strakosch, B 5, 698) p-NITRO-BENZYL SULPHOCYANIDE C.H.(NO.) CH.SON. Formed from p natrobenzyl chloride and alcoholic potassium sulpho cyanide (Henry, B 2, 638) Small needles

p NITRO - BENZYL - DI - THIO - CARBAMIC ACÍD NO, C,H, CH, NH CS SH The p nitro benzyl ammonium salt [193°] of this acid is formed by treating p nitro benzylamine with CS_2 in ether (Hafner, B 23, 339)

DI p-NITRO-DI-BENZYL-THIO-UREA $CS(NHCH_2.C_6H_4NO_2)_2$ [202°] Formed by boiling p-nitro benzyl ammonium p nitro Formed by benzyl di thio carbamate with HgO and alcohol (Hafner, B 23, 840) Needles, sl sol alcohol

o NITRO-BENZYL p TOLUIDINE C₆H₄(NO₂) CH₂ NH C₆H₄Me [72°] Obtained by heating 4 pts of p toluidine with 1 pt of o-nitro benzyl chloride for 1 hr on the water bath Yellow crystals V sol most ordinary solvents

Salts - B'HCl colourless needles B',H PtCl, * sparingly soluble pp -B',H,SO,* thin glistening plates

Acetyl derivative

C₆H₄(NO₂) CH₂ NAcC₆H₄Me [65°], stout crys tals, on reduction with tin and HCl it is converted into o amido benzyl toluidine (Lellmann a Stickel, B 19, 1609, 24, 718)

Formyl derivative [79°] Formed by heating a solution of formyl p toluidine in benzene with sodium till dissolved, and then adding p nitro benzyl chloride (Paal a Busch, B 22, 2695) Needles

o Nitro benzyl o toluidine Formyl deri vative C,H,(NO2) CH, N(C H,) CHO Formed from o nitro benzyl chloride and sodium formyl o-toluidine (Paal a Busch, B 22, 2701) Yellow needles grouped in spherules

p NITRO BENZYL UREA C₈H₉N₃O₃ NH, CO NH CH, C, H, NO [197°] Formed by heating p nitro benzylamine hydrochloride with silver cyanate at 100° (Hafner, B 23, 339) Pale yellow needles, v sol HOAc and alcohol

DI p-NITRO DI-BENZYL UREA CO(NH CH2 C4H4NO2)2 $CO(NH CH_2 C_6H_4NO_2)_2$ [234°] Formed by boiling the corresponding this ures with H_6O , or by adding a solution of COCl2 in benzene to one of p nitro benzylamine in ether (Hafner, B 23, 340) Silvery needles (from HOAc)

NITRO BROMO compounds v Bromo NITRO COMPOUNDS

NITRO BRUCINE v BRUCINE

ω NITRO-n BUTANE C,H,NO, : 6 CH, CH,CH,CH, NO, (152° cor) S G № 9945 Formed from n butyl iodide and AgNO, (Zublin, B 10, 2083, Pribram a Handl, M 2, 656) Re duced by tin and HCl to butylamine HClAq at 140° forms hydroxylamine and n butyric acid

8 Nitro butane CH, CH, CH(NO,) CH, (188°) Formed from see butyl odde (120 pts) and silver nitrite (150 pts) (V Meyer a Locher, B 7, 1506, A 180, 134) Formed also from CH₂ CHBrNO₂ and ZnEt₂ (Bevad, J R 20, 125) S-Nitro isobutane (CH₂)₂OH CH₂NO₂ (137°-144°) S G 2 10088 Formed from see isobutyl children and ApNO (Demole R 7, 700, 700)

nodde and AgNO, (Demole, B 7, 709, 790, A 175, 142, P a H) Unlike ω nitro n butane, it does not give a crystalline pp with NaOEt, although it dissolves in alkalis

Nitro tert-butane (CH3), CNO2 (110°-180°) Formed, in small quantity, together with tert butyl nitrite, by the action of AgNO, on tert butyl nodide (Tschermak, A 180, 155) Oil, smelling like peppermint Does not dissolve in Aor III

alkalis May be reduced to tert butylamine (cf V Meyer, A 244, 222)

Di-nitro-butane C.H.N.O. Formed from bromo ω nitro n butane, aqueous KNO₂ and dilute H₂SO₄ (Zublin, B 10, 2085) Oil, decomposed at 190° by distillation — KC₄H,N,O₄ golden scales, sol water and alcohol — AgC4H7N2O4 yellow scales with blue reflex

Di nitro butane C₄H₈(NO₂)₂ (197°) 15 1.205 Formed by the action of HNO, on di isoamyl ketone or on propyl acetoacetic ether (Chancel, C R 94, 399, 96, 1466) Heavy oil, forming crystalline K and Ag salts Decom posed on distillation

D1-(β)-nitro-butane CH, CH, C(NO,), CH, (199° cor) Formed by oxidising butyl ψ nitrole with nitric acid (V Meyer, B 9, 701), or by boiling isovaleric acid with HNO, (Bredt, B 15, 2324) Oil, not soluble in alkalis Tin and HCl convert it into hydroxylamine and methyl ethyl ketone

Di-nitro-isobutane (CH₃)₂CH CH(NO₂)₂ Formed from bromo nitro-isobutane, KNO2, and dilute H,SO, (Z) Oil — KC,H,(NO,), — AgC,H,(NO,), laq DI-NITEO-ISOBUTYL-ANILINE C, H, IN,O,

[80°] Formed from ie and isobutylamine te C₄H₉NH C₆H₃(NO₂) bromo m di nitro benzene and (Romburgh, R T C 4, 192) Yellow needles Tri nitro isobutyl aniline

C.H.(NO.),NHC.H. [95°] Formed chloro tri nitro benzene (picryl chloride) and isobutylamine (R) Converted by fuming HNO₂ into the nitramine C₂H₂(NO₂)₂N(NO₂)C₄H₂ [110°] m NITRO ISOBUTYL BENZENE C₁₀H₁₃NO₂

1 c C₆H₄(NO₂) C₄H₉ (251°) at 740 mm Formed from nitro amido isobutyl benzene by elimina tion of NH₂ (Gelzer, B 21, 2941) Oıl Yields m nitro benzoic acid on oxidation

o Nitro-tert butyl benzene C.H.(NO) CMe, [12] (249°) SG 15 1074 Formed from tert butyl benzene and fuming HNO, (Senkowsky, B 23, 2416) Yellow oil, Smelling like cymene Reduced by tin and HCl to C₈H₄(NH₂) CMe₃, (c 235°), S G 15 977, which yields an acetyl derivative [159°]

p-Nitro-tert-butyl benzene $C_{e}H_{\bullet}(NO_{s}) CMe_{s}[1 \ 4] [30^{\circ}]$ (276°)Formed at the same time as the preceding (S) Yields, on reduction, needles (from alcohol) C₄H₄(NH₄) CMe₃ S G 15 953 NITRO m ISOBUTYL BENZOIC ACID

C_eH_s(C_tH_s)(NO)CO_tH [140°] Formed by nitra tion of m isobutyl benzoic acid (Kelbe a Pfeiffer, B 19, 1727) Small needles (from petroleum ether)—AgA' somewhat soluble pp—MeA' lıquıd

Natro p asobutyl benzoic acid C.H. (C.H.) (NO2) CO2H [161°] Long fine needles (from water) Formed by nitration of p isobutyl benzoic acid -AgA' white pp

Methyl ether MeA' fluid (Kelbe a.

Pfeiffer, B 19, 1726)

NITRO-BUTYLENE C.H.NO. (154°-158°)
Formed by allowing HNO. (S G 152) to drop into tert butyl alcohol (Haitinger, Sits W 77
[2] 428, A 158, 366, M 2, 286) Formed also (154°-158°) in small quantity by saturating HNO, with iso butylene (H) Pale yellow oil, heavier than butylene (H) Pale yellow oil, heavier than water Dissolves in alkalis, and is reppd by acids. Excess of water at 100° splits it up into scetone and nitro methane Br unites, forming only C₄H₂Br₂NO₂.—NaC₄H₅NO₂ powder, v sol water

NITRO ISOBUTYL-PHENOL

C.H., C.H., (NO.) (OH) [1 3 4] [95°] (290°) at 711 mm Formed by boiling nitro amido isobutyl benzene with dilute potash (Gelzer, B 21,2947) Red needles (from alcohol), v sol hot water

Bi-nitro isobutyl-phenoi C₄H₂ C₆H₂(NO₂)₂OH [98°] Formed from isobutyl phenol [99°], HOAc, and HNO₈ (Studer, A 211, 244, B 14, 1474, Liebmann, B 14, 1842) Sulphur yellow needles (from alcohol) Yields di nitro amido isobutyl benzene on heating with NH₂Aq

TRI-NITEO-ISOBUTYL-TOLUENE

J_aHMe(O,H_a)(NO₂)_s Artificual musk [97°]
Formed by heating isobutyl toluene with HNO₄ and H_aSO₄ for 24 hours on a water-bath (Baur, J R 111, 238) White needles, sol alcohol and ether Its solutions smell like musk Forms a crystalline compound with naphthalene [90°]

TRI NITRO ISOBUTYL XYLENE

0₆Me₂(O₄H₂)(NO₂)₈ [110°] Formed by nitra
non of isobutyl xylene (Baur, C R 111, 238)

White needles Its alcoholic solution smells like
musk

NITRO-CAMPHOLENIC ACID v CAMPHO-LENIC ACID

NITRO-CAMPHOR v CAMPHOR TETRA NITRO CARBAZOLE

C_{1,}H_s(NO₂)₄NH Formed by nitrating carbazole (Graebe, A 202, 26) Lemon yellow crystals (from HOAc), insoluble in alcohol and ether—C_{1,2}H_s(NO₂)₄NK insol water

Four tetra-nitro carbazoles have been de scribed by Ciamician and Silber (G 12, 277) as formed by the nitration of carbazole. The melting points of three of them are 308°, above 320°, and about 285°, while the fourth decomposes before melting

NITRO CARBOXY CINNAMIC ACID

C₅H₅(CH CH CO,H)(NO₂)(CO,H)[1 2 4] [287°]

(Lów, A 281, 371) Formed by nitrating carboxy cinnamic acid Hemispherical aggregates or regular tablets (from water) That the NO₂ is in the o position is shown by the fact that, by Baeyer's synthesis, it gives rise to indigo di carboxylic acid Heated with cone H₂SO₄ it does not turn blue It yields a dibromide, which is converted by aqueous NaOH into intro carboxidation.

oxy phenyl-propiolic acid NITRO-CARBOXXY-PHENYL-PROPIONIC ACID C₀H₄(NO₂)(CO₂H)CH CH CO₂H [3 1 4]? [192°] Got by nitration (Widman, B 22, 2273)

[192°] Got by nitration (Widman, B 22, 2273)

NITRO-CARVACROL O, H, NO, ve
C, H_(C, H,) Me(NO,) (OH) [78°] Formed from nitroso carvacrol, KOH, and K, FeCy, (Paterno a Canzoneri, G 10, 233) Needles, almost insolwater

NITRO-CHLORO-derivatives v Chloro-Nitroderivatives

NITRO-CHLOROFORM v TRI-CHLORO-NITRO-

DI-NITRO-CHOLESTERIN C₁₂H₁₂(NO₂)₂O [121°] Obtained by intration of cholesterin (Preis a Raymann, B 12, 224) Colourless needles, si sol cold alcohol. By boiling a hot saturated solution of cholesterin in HOAc with HNO₂ (S G 154), Reinitzer (M 9, 440) obtained a nitro compound melting at 94° By adding cholesterin (1 pt) to a mixture of HOAc (10

pts) and fuming HNO_s (3 pts), Latschinoff (J R 10,360) obtained a compound crystallising in plates, decomposing at 180° without melting

NITRO CHOLESTERYL CHLORIDE

C_bH₄₂(NO₂)Cl [148°-149°] Colourless needles

Prepared by nitration of cholesteryl chloride

(Preis a Raymann, B 12, 225)

NITRO CHRYSENE v CHRYSENE

NITRO-CHRYSOQUINONE v CHYSOQUINONE NITRO-CINCHONAMINE v CINCHONA BASES O-NITRO CINNAMIC ACID C₂H,NO₄ v e [2 1]C₂H₄(NO₂) CH CH CO₂H Mol w 193 [232°] (M), [237°] (T a O), [240°] (Baeyer, B 13, 2257) Formed, together with the p isomeride, by nitrating cinnamic acid (Beilstein a Kuhlberg, A 163, 126, Muller, A 212, 124) Formed also from o nitro benzoicaldehyde, Ac₂O, and NaOAc (Gabriel a Meyer, B 14, 830)

Preparation —1 Cinnamic acid (1 pt) is dissolved in nitric acid (5 pts), the mixture is poured upon snow, and the ppd acids separated by means of alcohol (B a K) —2 Cinnamic ether (10 g) is dropped into fuming $\mathrm{HNO_3}$ at 0° The solution is poured at once into water at 0° The solution is poured at once into water at 0° The solution piece was head with water, and treated with alcohol, which dissolves the o, leaving the p compound (Stuart, C J 43, 408) Fair yield (4 g) —3 The product of nitration of oinnamic acid is etherified, and the o nitro cinnamic ether is separated from the p isomeride by means of its greater solubility in ether (Tiemann a Oper mann, B 13, 2060) The acid may then be obtained from its ether by hydrolysis with $\mathrm{H_2SO_4}$ (Fischer a Kuzel, A 221, 265)

Properties — Needles, insol water, sl sol cold alcohol Yields o intro benzoic acid on oxidation by chromic acid inixtuie. Its solution in H₂SO₄ becomes blue on warming or on standing

Salts — CaA', 2aq yellow needles — BaA', 4aq minute yellow needles

Methyl ether MeA' [73°] Ethyl ether EtA' [42°] (M), [44°] (B) Trimetric crystals, abc = 9271 517 Readily combines with bromine Reduced by aqueous ammonium sulphide to carbostyril In hot al coholic solution tin and HCl reduce it to a annido cinnamic ether

Chloride C₆H₄(NO₂) CH CH COCl [65° Crystalline solid (Fischer a Kuzel, B 16, 34)

m Nitro cinnamic acid
[3 1]C₆H₁(NO₂) CH CH CO₂H [197°] Prepared
by heating m-nitro benzoic aldehyde with Ac₂O
and NaOAc (Schiff, B 11, 1783, Tiemann a
Opermann, B 13, 2060) Yellow needles Yields
m nitro benzoic acid on oxidation A mixture
of HNO₃ (2 pts of SG 15) and cone H₂SO₄
(5 pts) converts it at 0° into ωm di nitro styrene
(Friedlander a Lazarus, A 229, 283) Reduced
by tin and HCl to m amido cinnamic acid.—
AgA' insoluble pp

Ethyl ether EtA' [79°

p-Nitro cinnamic acid
[4 i] C₈H₄(NO₂) CH CH CO₂H [286°] (T a O),
[288°] (D) Formed by nitration of cinnamic
acid (Mitscherlich, A Ch. [8] 4, 73, E Kopp,
C R 53, 634, Tiemann a. Opermann, B 18,
2059)

Preparation — From cinnamic acid (1 pt) and cold HNO₂ (5 pts) The acids produced are etherified, the p ether, [189°], crystallising from

alcohol It is saponified by H2SO4 (1 pt), HOAc (1 pt), and water (1 pt) (Drewson, A 212, 150) Properties — Prisms, v sl sol boiling alco-Yields p-oxy-benzoic acid on oxidation Salts—KA' very soluble crystals—

Salts – KA' very soluble orystals –
CaA', 8aq — CaA', 2aq — SrA', 5aq — BaA', 3aq
mnute needles – MgA', 6aq nodules – HgA', –
Hg, A', Cl, 3aq – AgA' msoluble pp
Methyl ether MeA' [1617] (286°)

Methyl ether MeA' [1619] (286°) Ethyl ether EtA' [139°] (B a K), [137°] (Muller, A 212, 125) Combines with bromine forming a dibromide whence alcoholic potash produces two bromo nitro cinnamic ethers, melting at 63° and 93° Reduced by tin and HCl to p amido cinnamic acid and p-amido-styrene (Bender, B 14, 2359)

Anhydride (C₆H₄(NO₂) CH CH CO)₂O Formed from the K salt and POCl, (Chiozza, A Ch [2] 39, 231) Melts under boiling water Amrde C₆H₄(NO₂) CH CH CONH₂ [155°-160°] (Cahours, A Ch [3] 27, 452)

a m Di-nitro-cinnamic ether Formed from m C₆H₄(NO₂) CH C(NO₂) CO₂Et nitro cinnamic ether, HNO, (1 pt) and HSO, (2 pts) below 20° (Friedlander a Lazarus, A 229, 235) Thick plates (from ether) water and light petroleum

Reactions -1 With alcohol, on warming, it forms C₀H₄(NO₂) CH(OEt) CH(NO₂) CO₂Et, a colourless oil When this is dissolved in ether and ammonia is passed in, a pp of C₀H₄(NO₂) CH(OEt) C(NH₄)(NO₂) CO₂Et is This is soluble in water and gives pps with many metallic salts The compound C₆H₄(NO₂) CH(OEt) CH(NO₂) CO.Et is converted by the simultaneous action of bromine and NaOH into the ethyl derivative of di bromo di nitro a phenyl methyl carbinol -2 Boiled with water it forms alcohol, nitro methane, CO2, and m nitro benzoic aldehyde

ap Di nitro cinnamic acid [4 1] C₆H₄(NO₂) CH C(NO₂) CO₂H Formed from p nitro cinnamic acid, HNO₃, and H₂SO₄ at -10° to -20° White plates At 0° it decomposes into CO, and ap di nitro styrene

Methyl ether MeA' [127°]

Ethyl ether EtA' [110°] Formed from p nitro cinnamic ether (1 pt), HNO, (2 pts of $S \in \{15\}$, and H_2SO_4 (4 pts.) (Friedlander a Mahly, A 229, 210) Thin plates (from benzene ligroin), v sol benzene, nearly insol ligroin

Reactions —1 CrO₄ in HOAc exidises it to p nitro benzoic acid —2 K₂Cr₂O₇ and HOAc forms p nitro benzoic aldehyde —3 Boiling water decomposes it into alcohol, CO2, p nitro benzoio aldehyde, and nitro methane Boiling dilute soids behave in the same way, only the nitromethane appears as hydroxylamine -4 A solu tion in conc H2SO4 at 100° poured into water gives a pp of p nitro benzaldoxim - 5 Boiling dilute (5 pc) Na, CO, forms bright yellow plates of C₁₄H₁₀N₄O₅ [188°], insol water, dilute acids, and alkalis - 6 Alcohol unites forming C_eH₄(NO₂) CH(OEt) CH(NO₂)CO₂Et[52°], whence the alcohol cannot be removed by heating at 110°, or even with dilute HOI at 90° Methyl alcohol forms the corresponding C₆H₄(NO₂) CH(OMe) CH(NO₂) CO₂Et 7 Tin and HCl reduce it to ap-diamido-phenylpropionic ether and p-amido phenyl-acetonitrile

o NITRO CINNAMIC ALDEHYDE C.H.NO. *.e [2 1] C₈H₄(NO₂) CH CH CHO [127°] Formed by boiling o nitro oxy phenyl propionic aldehyde with Ac₂O (Baeyer a Drewson, B 16, 2207) Formed also by condensation of o nitro benzoic aldehyde with aldehyde by means of dilute NaOH, the yield being 40 p.c. of the theoretical (Diehl a Einhorn, B 20, 2335)

Preparation —25 g of cinnamic aldehyde are slowly added to 500 g of conc H2SO4 containing 20 g of KNO. The solution is precipitated in water, and the mixture of o- and p nitro cinnamic aldehydes is crystallised from alcohol with animal charcoal The product is dissolved in absolute alcohol and the boiling solution mixed with an equal volume of sodium bisulphite solution, the solution is quickly cooled and separates the greater part of the bisulphite compound of the p isomeride, the remaining portion being salted out by the addition of NaCl, the filtrate contains the bisulphite of the o-isomeride The two isomerides are obtained from their bisulphites by decomposing the latter in aqueous solution with H2SO4 (Diehl a Einhorn)

Properties - Colourless needles, v sol boiling water and CHCl3, sl sol alcohol and ether Combines with bisulphites Yields quinoline on reduction On heating with malonic acid in HOAc it yields C₆H₄(NO₂) CH CH CH(OH) CH(CO₂H)₂ [269°] and o nitro phenyl butinene dicarboxylic acid C12H,NO [213°] (Einhorn a Gehrenbeck,

A 253, 374)

Phenyl hydraside C₆H₄(NO) CH ČH CH N₄HPh [158°] Needles

Di phenyl hydrazide C₆H₄(NÔ₂) CH CH ČH N₂Ph r69°1 Yellow crystals (Cornelius a Homolka, B 19, 2240)

m Nitro cinnamic aldehyde C₈H₄(NO₂) CH CH COH [116°] Formed by eliminating H₂O from m nitro β oxy β phenylpropionic aldehyde (Göhring, B 18, 720) Prepared by dissolving 100 pts of m-nitro benzaldehyde in 2,000 pts of alcohol, diluting with 4,000 pts of water, and adding at once to the milky liquid 35 pts of coml acetic aldehyde and 70 pts of 10 pc aqueous NaOH After 12 hours' standing the pp is separated, pressed, washed, and crystallised, the yield is 50 pc of the theoretical (Kinkelin, B 18, 483) Long thin prisms, sol benzene and acetic acid, sl sol cold alcohol, ether, and hot water Unites with Br forming

C.H.(NO.) CHBr CHBr CHO [c 90°]

Phonyl hydraside
C.H.(NO.) C.H.CH N.HPh [100°], red tables.

p-Nitro-cinnamic aldehyde [142°] [4 1]C,H,(NO,) CH CH CHO from p-nitro benzoic aldehyde, aldehyde, and dilute NaOH, the resulting p nitro \$\text{8}\ \text{oxy-\$\text{\$\beta}\$}, \text{ Binhorn, \$A\$} = \$18, 372, Einhorn, \$A\$ 258, 348) Formed also, together with the o isomeride, by nitration of cinnamic aldehyde (v supra) Colourless needles Combines with bisulphites Condenses with acetone in presence of NaOH to (O.H.(NO.) CH CH CH CH), CO [218°] and C.H.(NO.) CH CH CH CH CO CH, [182°], the last compound forming a phenyl-hydrazide melt ing at 210° Oxim CoH4(NO2) CH CH.OH(NOH) [179°]

Phenyl-hydraside [1819]. Orange C.H.(NO.) C.H. CH N.HPh.

red crystals, forming a red solution in cone

Anilide CeH4(NO2) CH3 NPh [183°] o-NITRO-CINNAMOYL - ACETO ACETIC

ETHER C₁₈H₁₈NO₆ te C₆H₄(NO₂) CH CH CO CHAc CO₂Et [120°] Pre pared by the action of o nitro cinnamoyl chloride on sodio-acetacetic ether (Fischer a Kuzel, B 16, 84) Yellow prisms Sol chloroform, sl sol alcohol and ether It forms stable salts with alkalıs, soluble in water with a reddish-yellow colour Gives a dark red colouration in alcoholic solution with Fe₂Cl₆ Boiled with 30 p c dilute H2SO4 it gives nitro cinnamoyl acetone

o NITRO-CINNAMOYL ACETONE C.H.(NO.) CH CH CO CH. CO CH. [118°] Prepared by boiling o mitro cinnamoyl-aceto acetic ether with dilute H SO (30 p c) By longer boiling with dilute H2SO, it is converted into o nitro-(o-nitro benzylidene styryl-methyl ketone acetone) (Fischer a Kuzel, B 16, 85) Fine yellow prisms Sol hot alcohol, sl sol cold alcohol, ether and CS, Gives a red colouration with Fe₂Cl₈ Dissolves in alkalis with a yellow colour

NITRO-COCCUSIC ACID v TRI-NITRO OXY-m-TOLUIC ACID

NITRO-CODEÏNE v CODRINE

NITRO-COMENIC ACID v Comenic acid

NITRO-COMPOUNDS Compounds containing the group nitroxyl (NO2) directly united, by means of its nitrogen, to carbon Their most general characteristic is that they yield amido compounds on reduction (v Amines and Amino ACIDS)

Formation -1 Fatty nitro compounds are formed by the action of silver nitrite on alkyl iodides The isomeric nitrites are also formed in this reaction -2 Aromatic nitro compounds are formed by the direct action of nitric acid nitric acid must usually be concentrated, and its action is intensified by mixture with H,SO. Phenols and oxy acids may be nitrated by dilute Various anilides, boiled with dilute nitric acid nitric acid (SG 1029), are converted into di nitro derivatives of the base Thus acetyl methyl-aniline becomes di nitro methyl aniline (Norton a Allen, B 18, 1995) -3 Aromatic amido compounds may be converted into the corresponding nitro compounds by the cuprous reaction (Sandmeyer, B 20, 1495) For this purpose cupric sulphate (50g) is dissolved, together with glucose (15g), in boiling water (100 cc), and at once treated with soda (20g) dissolved in water (60 c c) After cooling, the mixture is neutralised with acetic acid mixture the nitrate of the diazotised base (pre pared from the base, HNO, and NaNO, is added in the cold -4 Fatty compounds of the form X CHBr NO, are converted by KNO, in alkaline solution into salts of di-nitro compounds of the form X OK(NO₂)₂.

Reactions —1 Acid reducing agents yield

amido compounds directly, but alkaline reducing agents (e g sodium amalgam, zinc-dust and NaOH) acting upon aromatic nitro compounds yield in the first place intermediate bodies, v Azo- and Azoxy- compounds In some cases where reduction is effected by tin and HClAq chlorination may take place, thus m nitrotoluene gives a chloro-seluidine The best

general reducing agent is a solution of SnCl2 in HClAq -2 In the groups CH, NO, and CH NO, hydrogen is displaceable by metals, and hence bodies containing these groups dissolve in alkalis Such solutions yield, on addition of bromine, compounds containing the groups CHBr NO, and CBrNO, The compounds X CHBrNO₂ can further give rise to X CNaBrNO₂ and X CBr2NO2-3 Primary fatty nitro compounds yield hydroxylamine on heating with HClAq at 140°, eg CH₂CH₂NO₂+H₂O = CH₂CO OH + H₂NOH (V Meyer a Locker, A 180, 163) -4 Nitrous acid converts primary fatty nitro compounds into nitrolic acids, con taining the group CH(NO)(NO2) or C(NOH) NO2, which form red solutions with alkalis Nitrous acid converts secondary fatty nitro compounds into nitroles, containing the group C(NO)(NO₂), which are blue when in the liquid state or in solution -5 Aromatic nitro compounds may be reduced by heating with halogen acids Thus nitro benzene is reduced to aniline by heating with HIAq at 104°, by HBrAq at 185°, and by HClAq at 245° (Baumhauer, A Suppl 7, 212) -6 Boiling aqueous alkalis can in some cases displace NO₂ by hydroxyl In this way o di nitro benzene is converted into o nitro phenol -7 When aromatic compounds containing two or more nitroxyls in one benzene nucleus are treated with alcoholic NH, and H2S it is usual for one nitroxyl only to be reduced to amidogen -8 Aromatic di and tri nitro compounds fre quently form molecular compounds with one another and with aromatic hydrocarbons 9 The acetyl derivatives of nitrated aromatic amines, in which the NO2 group is in the o- or p position to the NHAc group (e g acetyl o and p nitro aniline, di acetyl nitro p phenylene diamine, diacetyl nitro p naphthylene diamine, acetyl o nitro β naphthylamine, &c), are readily soluble in cold aqueous KOH(12) with a deepyellow colour On standing saponification takes place, and the nitro compound crystallises out When the NO₂ group is in the m position to the NHAo group, eg acetyl m nitraniline, acetyl m nitro p toluidine, &c., the substance is not soluble in aqueous KOH (Kleemann, B 19, 836)

NITRO o COUMARIC ACID Methyl derivative C10H0NO, i e $[5\ 2\ 1]\ C_s H_s (NO_2) (OMe)\ CH\ CH\ CO_H$ Formed by heating C₆H₃(NO₂)(OMe) CHO with NaOAc and Ac₂O (Schnell, B 17, 1883) needles, sl sol cold water, v sol alcohol and ether —CaA'2.—BaA'2 —AgA

Anhydride C,H3(NO2) CH CH OO [183°] Formed by dissolving cou marin in cold fuming HNO, (Delalande, A Ch [3] 6, 343, Bleibtreu, A 59, 191) Formed also by heating nitro salicylic aldehyde [125°] with Ac.O and NaOAc (Taege, B 20, 2110) Needles

Natro-

Oxidised by KMnO, to nitro o oxy benzoic acid [228°] Reduced by FeSO, and NH, to amido coumarın [161°] Bromine vapour gives a di bromide [271°]

Nitro-o-coumarie soid C.H.NO. s.e [8 2 1] O.H. (NO.) (OH) CH CO.H [242°] Formed by heating its methyl derivative with NaOHAq Yellow crystals (from alcohol) Not NaOHAq Yellow crystals (from alcohol) Not converted into nutro-commarm by boiling water

or by HBrAg.

Methyl derivative C₆H₃(NO₂)(OMe) CH CH CO₂H [193°] Formed from the methyl derivative of (3,2,1)-nitro salicylic aldehyde by Perkin's reaction (Miller a Kinkelin, B 22, 1709) Prisms (from alcohol) With methyl iodide it gives the ether C₆H₃(NO₂)(OMe) CH CH CO₂Me [89°]

Nitro-o coumarinic acid [3 2 1] C_eH₃(NO₂)(OH) CH CH CO₂H Formed by dissolving nitro coumarin in boiling aqueous alkalıs, and ppg the cold solution by HCl (Miller a Kinkelin, B 22, 1706) Yellow prisms (from warm alcohol) On warming with water or alcohol it changes to its anhydride, nitro coumarın Its salts are explosive — $Na_2O_bH_bNO_b$ — $BaC_9H_bNO_53$ aq — $Ag_2O_9H_bNO_b$

Methyl derivative

C.H.(NO2)(OMe) CH CH CO.H [136°] Tables Methyl derivative of the methyl Formed from the ether Me C₉H₅NO₅ [69°] Formed from the Ag salt and MeI Prisms Readily reconverted into the acid, even by aqueous Na, CO,

Anhydride C,H,(NO2) CH CH OO Nitro ୮191°1 Formed from (3,2,1) nitro coumarın salicylic aldehyde (60g), NaOAc (90g), and Ac₂O (130 g) Prisms (from benzene), or needles (from alcohol)

Nitro m coumaric acid $[2\ 3\ 1]\ C_6H_3(NO)(OH)\ CH\ CH\ CO_2H$ Formed from mamido cinnamic acid by nitra tion and displacement of NH by OII through the diazo reaction (Luff, B 22, 293) Needles (from

water or alcohol)

Nitro m coumaric acid [4 3 1] C₆H₃(NO₂)(OH) CH CH CO₂H [248° Formed by nitrating m coumaric acid (Luff, B Golden yellow needles (from alcohol)

Methyl derivative C_eH₃(NO₂)(OMe) CH CH CO H [218°] Formed from [4,3,1] C, H, (NO) (OMe) CHO by Perkin's reaction (Landsberg, D P J 262, 139)

Methyl ether of the methyl derivative C_eH₁(NO₂)(OMe) CH CH CO₂Me [143°] Plates (Rueche, B 22, 2359) Formed by nitra-Formed by nitration of C₆H₄(OMe) CH CH CO₂Me

Ethyl ether of the methyl deri vative C₈H₃(NO₂)(OMe) CH CH CO₂Et [163°] Needles (from alcohol) (Ulrich, B 18, 2572)

s-Nitro m coumaric acid [5 3 1] C₆H₃(NO₂)(OH) CH CH CO₂H Accom panies the (2,3,1) acid (v supra) Crystals

Nitro m coumaric acid [6 3 1] C₆H₃(NO₂)(OH) CH CH CO₂H Formed from acetyl m amido cinnamic acid by nitration and displacement of NHAc by hydroxyl (Luff, B 22, 292) Yellow powder

Nitro p coumaric acid [3 4 1] $C_8\tilde{H}_4(NO_2)(OH)$ CH CH CO_2H Formed from its methyl derivative by heating with HOAc saturated with HBr (Einhorn a Grabfield, A 243, 374) Yellow needles (from alcohol) Forms a dibromide [72°].

Ethyl ether Eth' [109°]

Methyl derivative C₄H₃(NO₂)(OMe) CH CH CO₂H [140°] Formed from [8 4 1] C.H.(NO.)(OMe) CHO, NaOAc, and Yields a dibromide Ac,O White needles from which alkalis form the acid 178° C.H.(NO.)(OMe) C.HBr.CO.H [205°].

Methyl ether of the methyl derivative C₆H₁(NO₂)(OMe) CH CH CO₂Me Ethyl sther of the methyl vative C₆H₁(NO₂)(OMe) CH CH CO₂Et [125°] ders [100°]

Di-nitro-o-coumaric acid Methyl ders. vative CeH2(NO2)2(OMe) CH CH CO2H [193°] Formed by nitrating the methyl derivative of ocoumaric acid (Perkin, C J 89, 416) Orangebrown needles (from alcohol)

Di nitro-m-coumaric acid Methyl ders vative of the methyl ether $C_0H_2(NO_2)_2(OMe)$ CH CH.CO₂Me [178°] Formed by nitration (Rieche, B 22, 2358) Yellowish needles (from alcohol) Yields on saponification C₈H₂(NO₂)₂(OMe) CH CH CO₂H, which decomposes at 215°

NITRO-O COUMARIC ALDEHYDE

 $C_sH_3(NO_2)(OH)$ CH CH CHO [200°] Formed from $C_sH_3(NO_2)(OH)$ CHO [126°], aldehyde, and aqueous NaOH (Von Miller a Kinkelin, B 20, 1931, 22, 1716) Yellow needles Forms a sodium derivative, crystallising in red tables, and a phenyl hydrazide [235°

Nitro-o coumaric aldehyde [3 2 1] O,H,(NO,)(OH) CH CH CHO [133° Formed in the same way from the aldehyde C₀H₃(NO₂)(OH) CHO [109°] (M a K) Golden needles, v sol alcohol Forms a sodium deriva tive, crystallising in red needles, a phenyl hy drazide [157°], and a methyl derivative [115°]

NITRO COUMARIN v Anhydride of NITRO

COUMARIC ACID

NITRO-o-CRESOL C,H,NO, 16 $C_6H_3Me(OH)(NO_2)[1\ 2\ 3]$ [70°] Obtained, to gether with the (1,2,5) isomeride, by nitrating o cresol (Hofmann a Miller, B 14, 567, Staedel, A 217, 50, 203, Rapp, A 224, 175, Hirsch, B 18, 1512) Formed also by boiling a dilute acid solution of o diazotoluene sulphate (1 mol) with HNO_s (1 mol) (Nolting a Wild, B 18, 1839, Deninger, J pr [2] 40, 299) Yellow prisms (from dilute alcohol), insol water, v sol alcohol and ether, volatile with steam -KC, H, NO. garnet red trimetric tables -AgA' red needles Oıl

Methyl ether MeA' Oil E thy $oldsymbol{l}$ ether $\mathbf{E}\mathbf{t}\mathbf{A}'$

 $C_aH_2Me(OH)(NO_2)$ [1 2 4] Nitro-o cresol [108°] Formed by boiling diazotised nitro otoluidine [107°] with water (Nölting a Collin, B 17, 269) Yellow needles (from ligroin) Ag, and NH, salts form yellow crystals

Methyl ether [74°] (Witt, B 23, 3638) $C_6H_3Me(OH)(NO_2)[1 2 5]$ Natro o-cresol $[95^{\circ}]$ (N a W), $[80^{\circ}-85^{\circ}]$ (H) Formed from nitro o toluidine [128°] by the diazo- reaction, or by merely boiling with conc NaOHAq (Nevile a Winther, O J 41, 423) Formed also by nitra ting o cresol (Hirsch, B 18, 1512) Needles (from water), not volatile with steam When crystallised from water it melts at 30°-34°, but it melts at 95° after crystallisation from ether

Ethyl ether Eth' [71°] Formed by nitrating the ethyl derivative of o cresol (Staedel, △ 217, 155, 203, Kayser, B 15, 1133) Needles

 $C_0H_3Me(OH)(NO_2)$ [1 2 6] Nitro-o-cresol [148°] Formed from nitro o toluidine [92°] by the diazo reaction (Ulimann, B 17, 1961) Yellow needles (from water) Has an intensely sweet taste

c-Nitro-m-c-esol O.H.Me(OH)(NO.) [1 8 4] [56°] Formed, together with the (1,3,6) isomeride from m cresol, HOAc, and HNO, (Staedel, A 217, 51, A 259, 223, Claus, J pr [2] 39, 63) Yellow monoclinic plates (from benzene), volatile with steam Gives di bromo mitro cresol [93°] Its K salt forms red plates

Ethyl ether EtA' [51°] White needles

(from dilute alcohol)

s-Nitro-m-cresol $C_6H_2Me(OH)(NO_2)$ [1 3 5] [91°] Formed from nitro m toluidine by the diazo- reaction (Nevile a Winther, C J 41,417) Yellow crystals, not volatile with steam Crystal lises from water in a hydrated condition, and then melts at 62°

Nitro m cresol $C_6H_3Me(OH)(NO_2)[1 \ 3 \ 6]$ [129°] Formed, together with the (1,3,4) iso meride from m cresol, HNO3, and HOAc below 0° (Staedel, A 259, 210, Claus, J pr [2] 39, Formed also by oxidising nitroso m cresol with alkaline K₃FeCy₆ (Bertoni, G 12, 304) Colourless crystals, not volatile with steam Gives di-bromo nitro cresol [143°] Reduces to amido cresol [174°] -KA' 2aq yellow plates -NaA' 2aq

Ethyl ether EtA' [54°]

Nitro p cresol $C_6H_3Me(OH)(NO_2)[1\ 4\ 3]$ Formed from acetyl p toluidine by nitrating and boiling the product with conc NaOHAq (Wagner, B 7, 537, Nevile a Winther, C J 41, 426), by the action of nascent nitrous acid on p toluidine (Deninger, J pr [2] 40, 299), or by boiling p diazotoluene sulphate (1 mol) with HNO, (1 mol) (Nölting a Wild, B 18, 1339) Formed also by nitrating p cresol (Arm strong a Thorpe, B A 1875, 112, Hofmann a Miller, B 14, 572, Staedel, A 217, 54) Yellow crystals (from benzene), volatile with steam -NaA' -AgA'

Methyl ether MeA' (274°)

Ethyl ether EtA' (275°-285°) Bensylether C,H,A' [54°] Formed from benzyl chloride and the Ag salt (Frische, A 224,

o Nitro-benzyl ether [163°]

Nitro-p cresol $C_6H_3Me(OH)(NO_2)$ [1 4 2] [77°] Formed from the corresponding nitro ptoluidine by the diazo reaction (Nevile a Win ther, C J 41, 422, Knecht, A 215, 87) Yellow needles (from ligroin)

Methyl ether MeA' (267°)

D1 nitro o cresol C₆H₂Me(OH)(NO₂)₂[1 2 3 5] [86°] S (alcohol) 7 8 at 15° Formed by Formed by heating (1,2,5)-o-cresol sulphonic acid with dilute HNO₂ (Nevule a Winther, C J 37, 631, 41, 422) Formed also by boiling o diazo toluene disulphonic acid with dilute HNO₂ (N a W), or from o diazo toluene nitrate and HNO₂ (Nötling a De Salis, B 14, 987, A Ch [6] 4, 105) Ob tained also from the corresponding di nitro toluidine (N a S), and by nitrating o cresol and the (3,1,2)- and (5,1,2) nitro o cresols (Hirsch, B 18, 1512, Barr, B 21, 1543) Formed also from C₆H₂Me(OH)Br₂ and fuming HNO₃ (Claus, J pr [2] 38, 327) Yellow needles, slightly volatile with steam. Yellow dye -KA' xaq. yellow crystals

Salts —BaA'₂.—BaA'₂.3½aq —AgA' Ethyl ether EtA' [51°] Obtained by mitrating C₆H₄Me(OEt)[1 2] (Staedel, B 14, 899, A 217, 153, 259, 219), or from the Ag salt and EtBr (N a. 8). Yields di nitro-o toluidine

[210°] on heating with alcoholic NH, at 130° (Van Romburgh, R T C 8, 397)

p-Nitro-bensylether C,H,(NO2) CH2A' [145°] Obtained by nitrating the benzyl ether of o cresol (Staedel) Needles

Di-nitro-m-cresol

 $C_0H_2Me(OH)(NO_2)_2[1\ 3\ 4\ 5or2]$ [99°] Formed from d1-nitro-amido cresol by elimination of NH, (Nietzki a Ruppert, B 23, 3479) Needles. Ethyl ether Eth' [22°]

Di-nitro-m-cresol

 $C_0H_2Me(OH)(NO_2)_2$ [1 3 4 6] $Ethyl\ ether\ EtA'$ [9**7°**] Formed by nitrating ethyl-nitro-cresol [51°] (Staedel, A

 \mathbf{D}_1 -nitro p cresol $C_6H_2Me(OH)(NO_2)_2[1 4 3 5]$ A product of the action of nitrous acid on p toluidine nitrate, on amido toluic acid [167°], and on p toluidine disulphonic acid (Beilstein a Kreusler, A 144, 183, Martius a Wichelhaus, Z [2] 5, 440, B 2, 207, Richter, A 230, 323) Formed also by boiling di-nitro p toluidne with aqueous NaOH (Wagner, B 7, 536), by nitrating p cresol and (3,1,4) nitro p cresol (Armstrong a Field, B 6, 974, Frische, A**224, 139)**, or boiling diazo p toluene sulphonate with dilute HNO₈ (Nevile a Winther, C J 37, 631) Yellow needles (from dilute alcohol) – NaA' red needles S 23 at 17° – KA' S 15 at 16° (M a W), 99 at 17° (Staedel) Used as a dye (gold-yellow) A sample of 'Victoria yellow was found by Martius and Wichelhaus to consist of a salt of a dinitrocresol [110°] Victoria yellow is poisonous (Weyl, B 20, 2835)

—BaA'₂ —AgA' S 29 at 17°

Methyl ether MeA' [122°]

[122°] [73°] Formed by ni Ethyl ether EtA' trating ethyl p cresol (Staedel, A 217, 161) When heated with alcoholic NH, it yields di nitro p toluidine [168°] (Romburgh, R T C 3, 405)

Benzoyl ether C,H,A' [109°] p Nitro bensyl ether [186°

Di nitro p cresol CaH, Me(OH)(NO) tained by the action of excess of nitrous acid on $C_1H_3Me(OH)(NO_2)[1 4 2]$ (Knecht, A 215, 90) Yellow needles (from water) Does not melt when heated but forms a violet sublimate

Tri nitro o cresol C₆HMe(OH)(NO), [102°] Formed by heating nitro o diazo toluene nitrate with nitric acid (SG 133) (Nölting a Collin, B 17, 270) Orange prisms (from acetone) Yields NaNO₂ when heated with NaOHAq With naphthalene it forms (C,H,N,O,)C,0H, [106°

Tri nitro m-cresol

 $C_0HMe(OH)(NO_2)_s[1\ 3\ 2\ 4\ 6]$ [106°] S 2 2 at 20°, 8 at 100° (Duclos) Formed by nitration of m cresol or its sulphonic acid (Duclos, A 109, 141, Nölting a De Salis, B 14, 987, 15, 1861, A Ch [6] 4, 118, Beilstein a Kellner, A 128, 165) Formed also by the action of HNO₃ on nitroso m-cresol (Wurster a Riedel, B 12, 1799), by heating nitro coccusic acid with water at 180° (Luebermann a Dorp, A 163, 101, Kostanecki a Niementowski, B 18, 251), and by the action of cold cone HNO, on (2.6,3,4,1) diiodo-toluquinone (Kehrmann, J pr [2] 39, 892) Yellow needles (from water) Forms with naphthalene a compound (C,H,N,O,)C,oH, [127°] — NH.A' Converted by warm aqueous KCy into purple crystals of potassium 'cresyl purpurate' KC₉H₆N₅O₆ (Sommaruga, Z 1870, 657) —KA' prisms

yellow needles —Pb(OH)A' —AgA'
Ethyl ether EtA' [72°] (N
(Staedel, A 259, 221, 227) Conv [72°] (N a S), [75°] 7) Converted by cold alcoholic NH3 into tri nitro toluidine [126

NITRO O CRESOL SULPHONIC ACID

C,H,NSO, i e C,H,Me(OH)(NO,)SO,H Formed from (1,2,5) o toluidine sulphonic acid by dis solving in fuming HNO, and boiling the result ing nitro diazo toluene sulphonic anhydride with water (Hayduck, A 172, 218) Deliquescent $-\mathrm{BaC_7H_5NSO_6\,3_2^1aq}-\mathrm{Ba(C_7H_6NSO_6)_2\,5aq}$ Nitro p cresol sulphonic acid H

Ethylderivative C₆H₂Me(OH)(NO₂) SO₃H[1 4 2 5] Formed by heating nitro diazo toluene sulphonic acid with NaOEt (Foth, A 230, 306) Needles

-BaA', 4aq

BaA', 4aq yellow plates
NITRO CRYPTOPINE v CRYPTOPINE

NITRO CUMENE C₀H₁₁NO₂ te C₆H₄Pr(NO₂)

35°] Formed from cumene and fuming HNO, at 0° (Pospekhoff, J R 18, 52, Bl [2] 45, 178, cf Cahours, C R 25, 552, 26, 315, Nicholson, C J 1, 2, Ritthausen, J pr 61,79) Oil, volatile with steam

Nitro ψ cumene $C_0H_2Me_3(NO_2)[1\ 3\ 4\ 5]$ [20°] Formed by eliminating NH from nitro ψ cumidine (Edler, B 18, 629) Large thick

prisms, volatile with steam

Nitro ψ cumene 0ψ cumene $C_0H_2Me_3(NO_2)$ [71°] Formed from ψ cumene and cold $C_6H_2Me_3(NO_2)$ fuming HNO_s (Schaper, Z [2] 3, 12, Fittig a Laubinger, Z [2] 4, 577) Colourless needles (from alcohol), volatile with steam Yields on oxidation C, H Me (NO₂)CO₂H [195°]
Tri nitro cumene C₀H₃N₃O₆ ie
C₅H Pr(NO₂)₁[1 2 4 6] [109°] Formed from

cumene, HNO, and H SO, (Fittig, A 149, 328)

Needles, sl sol cold alcohol

Tri nitro ψ-cumene [185°] $C_{0}Me_{3}(NO_{2})_{3}$ Formed by nitrating ψ cumene (Fittig a Laubinger, A 151, 261) Prisms (from benzene), almost insol boiling alcohol By passing hydro gen sulphide into its boiling ammoniacal alco holic solution, nitro ψ cumidine sulphonic acid $C_8Me_s(NO_2)(NH_2)SO_8H$ [1 3 4 2 6 5] is formed (Mayer, B 19, 2312, 20, 966)

NITRO U CUMENOL

 $C_6HMe_3(OH)(NO_2)[1 3 4 6 2]$ [48°] Obtained by evaporating an alcoholic solution of the nitrate to dryness, and distilling the residue with steam (Auwers, B 17, 2979, 18, 2658) Long reddish yellow crystals (from alcohol), m sol hot water Reconverted into the nitrate by warming with dilute HNO

C₆HMe₂(NO₂) O NO Nitrate Formed from \(\psi \) cumenol and cold fuming HNO Trimetric tables or prisms, insol water, sl sol

cold alcohol

Methyl ether CeHMes(NO2)OMe Nitro-cumenol $C_6H_3Pr(NO_2)(OH)$ formed, together with an isomeride [86°], by nitrating C₆H₄Pr(OH)[1 2] (Fileti, G 16, 120)

Di-nitro-\psi-cumenol

 $C_6Me_3(OH)(NO_2)_2[1 \ 3 \ 4 \ 6 \ 2 \ 5]$ [112°] Formed by passing NH, into an alcoholic solution of the nitrate of nitro ψ cumenol [84°] Yellow crys tals, insol water Forms a red solution in alkalıs

NITRO CUMIDINE C,H,2N2O2 & C.H. (C.H.) (NO.) (NH.) [below 100°]. Formed

by reducing di nitro cumene with alcoholic am monium sulphide (Cahours, C R 24, 557, 26, Forms a crystalline 315) Yellow scales benzoyl derivative - B'HCl aq -B'2H2SO, aq. needles

Nitro \u03c4 cumidine

 $C_aHMe_*(NO_*)(NH_*)[13456]$ [47°] Formed from acetyl ψ cumidine by nitration and saponi fication (Edler, B 18, 629) Red needles (from dilute alcohol)

Acetyl derivative [194°] (E), [204°] (Auwers, B 18, 2661) Prisms (from alcohol)

Nitro- ψ -cumidine C₆HMe₃(NO₂)(NH₂) [137⁶ Formed by treating tri nitro ψ -cumene with alcoholic ammonium sulphide (Fitting a Laubinger, A 151, 262) Yellow needles -B'HCl -B'2H2SO4 aq

Nitro-\u03c4 cumidine Acetylderivative [131°] C₆HMe₃(NO₂)NHAc Formed by nitra tion of acetyl \(\psi \) cumidine [112°] (Engel, \(B \) 18,

2231) Yellow needles

Di-nitro ψ cumidine $C_6Me_3(NO_2)_2(NH_2)$ [78°] Formed from acetyl \(\psi \) cumidine [112°] by nitration and saponification (Engel, B 18, 2232) Yellow needles

Acetyl derivative [204°] Needles

Di nitro d cumidine

 $C_6Me_3(NO_2)_2(NH_2)$ [1 3 4 2 5 6] [183°] tained from acetyl v cumidine [164°] by nitration and saponification (Auwers, B 18, 2661) Orange needles (from alcohol)

[280°] Sl sol al-Acetyl derivative

NITRO \(\psi\)-CUMIDINE SULPHONIC

C₉H₁₀N SO₃ [1 3 4 2 6 5] 28 $C_6Me_s(NO_s)(NH_2)(SO_sH)$ Formed by passing H2S into a boiling solution of tri nitro v cumene in alcoholic NH_3 , and also by heating nitro ψ cumidine with ClSO, H at 165° (Mayer, B 19, 2312, 20, 966) Colourless plates position at 240°-260° Melts, with decom Forms an amorphous acetyl derivative C,H11AcN2SO, [o 230°]

C₁₀H₁₁NO₄ de Formed by NITRO CUMINIC ACID $C_6H_3Pr(NO_2)CO_2H[421]$ [99°] boiling nitro isopropyl cinnamic acid with CrO₃ in HOAc (Widman, B 19, 269) Tables or

monoclinic prisms

Nitro-cuminicacid C.H.Pr(NO.) CO.H[4 3 1] Obtained by nitration of cuminic acid (Gerhardt a Cahours, A Ch [3] 1, 73, 25, 36, Fileti, G 11, 15, Alexejeff, J R 17, 112, Bl [3] 2, 727) Formed also by oxidation of its aldehyde (nitro cuminol) [54°] (Lippmann a Strecker, B 12, 77, Widman, B 15, 2547) and of nitro cumyl methyl ketone (Widman, B 21, 2232) Yellowish scales (from alcohol), turned red by sunlight, especially when dissolved in benzene (Alexejeff, Bl [2] 45, 178) - CaA'2-PbA', —AgA'

Ethylether EtA' (290°) Oil
Nutrile C₆H₃Pr(NO₂) CN [71°] Formed
by nitrating cumonitrile (Czumpelik, B 2, 183) Formed

Nitro n cuminic acid

C.H.Pr(NO.) CO.H[431] [113°] Formed by oxidation of intro n cumyl methyl ketone by KMnO. (Widman, B 21, 2231) Formed also by nitration of n-cuminic acid (Korner, A 216, Colourless needles (from hot water), turned brown by light —BaA', 4aq — SrA', 5aq Methyl ether MeA' [64°] Crysta

Crystals from alcohol) (Abenius, J pr [2] 40, 438).

Natro n cuminic acid CaH2Pr(NO2) CO2H | [157°] Formed by oxidation of nitropropyl cinnamic acid (Widman, B 19, 276)
Tables (from dilute alcohol), sl sol water

Di nitro-cuminio acid C₆H₂Pr(NO₂)₂CO₂H [221°] Formed by nitration of cuminic acid (Cahours, A 69, 243, Lippmann a Strecker, B Reddish crystals -BaA'2 -CaA'2-AgA' aq (Kraut, C C 1859, 85)

Ethylether EtA' [7756]

Amede CoHo(NO2)2 CONH, Crystals

Di-nitro w cuminic acid CoMe1(NO2)2 CO2H $[205^{\circ}]$ Di nitro durylic acid **[184256]** Formed by nitrating ψ -cuminic acid (Gissmann, A 216, 207, Nef, A 237, 8) Prisms (from dilute alcohol) — CaA', 2 aq — BaA', 2 aq

NITRO CUMINIC ALDEHYDE C, H, NO, ve C_sH_sPr(NO_s) CHO [4 2 1] Nitro - cuminol Formed by oxidising nitro isopropyl cinnamic acid with KMnO₄ (Einhorn a Hess, B 17, 2019) Oil, volatile with steam With acetone 2019) Oil, volatile with steam and NaOHAq it produces di-isopropyl indigo

Nitro cuminic aldehyde CaH3Pr(NO2)CHO [431] [54°] Formed by nitration of cuminic aldehyde (Lippmann a Strecker, B 12, 76, Widman, B 15, 166) Triclinic prisms Com bines with bisulphites

NITRO U CUMOQUINONE O₂H₂NO₄ $C_6Me_3O_2(NO_2)$ [1 3 4 2 5 6] [113°] Formed by heating ψ cumoquinone carboxylic acid with HNO, (S G 14) at 100° for half an hour (Nef, C J 53, 428, A 237, 17) Yellow plates, which may be sublimed Heated with alcoholic SO2 in sealed tubes it yields $C_6Me_3(OH)_2(NO_2)$ [106°]

NITRO CUMYL ACRYLIC ACID v NITBO-PROPYL CINNAMIC ACID

NITRO CUMYL METHYL KETONE

C₁₁H₁₈NO₂ v e [1 2 4] C₆H₂Pr(NO₂) CO CH₈ Nitroaceto cumene [49°] Formed by nitrating cumyl methyl ketone in the cold (Widman, B 21, 2227) Prisms, v sol benzene, sl sol ligroin

 $Oxim C_aH_3Pr(NO_2) C(NOH) CH_3$ [117°]

Phenyl-hydrazide [138°] Nitro-n cumyl methyl ketone

[124] C₆H₃Pr(NO₂) CO CH₃ Formed by nitrating n cumyl methyl ketone (W) Oil

Oxim C₂H₁₀(NO₂) C(NOH) CH₃

Phenyl hydrazıde [139° NITRO-n-CUMYL-PROPIONIC ACID

C₆H₃Pr(NO₂) CH₂ CH₂ CO₂H[4 3 1] Formed by nitration (Widman, B 19, 2776) Crystals (from dilute HOAc)

NITRO-CYMENE C₁₀H₁₃NO₂ * 6 C₀H₃MePr(NO₂) [1 4 2] S G ¹⁵ 1 085 Formed by nitrating cymene (Barlow, A 98, 245, Landolph, B 6, 937, Fittica, A 172, 314, Widman, B 19, 584, Söderbaum a Widman, B 21, 2126) Yellow oil Oxidised by KMnO, to nitro oxyisopropyl benzoic acid and terephthalic acid

 $C_6H_2MePr(NO_2)$ [1 3 x] Nitro-isocymene Formed from m-isocymene and fuming HNO₃ (Kelbe a Warth, A 221, 161) Oil, volatile with steam, but decomposed on distillation Yields

nttro toluid acid [214°] on oxidation
Di nitro cymene C_cH₂MePr(NO₂)₂ [54°]
Formed by nitrating cymene (Kraut, 4, 92, 70) Got also from di-nitro amido cymene (Mazzara, G 19, 160) Indescent tablets (from alcohol)

Di-nitro-cymene [78°] Formed from di-nitroso cymene [72°] and HNO₂ (S G 1 35)

(Kehrmann a Messinger, B 23, 3562) v sol alcohol

D1 nitro-cymene $C_{10}H_{12}(NO_2)_2$ SG $\frac{18}{2}$ 1 206 Formed by nitrating cymene from ptychotis oil (Landolph) Oil, volatile with steam

Di nitro cymene $C_{10}H_{12}(NO_2)_2$ [250°] Got from a coal tar cymene (Rommier, Bl [2]19,434)

Tri-nitro-cymene C_sHMePr(NO_{.)} [119°] Formed by nitrating cymene (from camphor) (Fittig, A 145, 142) Thin plates

Tri nitro isocymene CaHMePr(NO2), Formed by nitration of m isocymene (Kelbe, A Yellow leaflets, smelling like musk

NITRO CYMENE SULPHONIČ ACID $C_6H_2MePr(NO_2)SO_3H[1 4 6 2]$ cymene by sulphonation and nitration (Errera, Ğ 19, 533) — BaA'2 aq — MgA', 5aq Amide [139°] Scales

Nitro-cymene disulphonic acid C₁₀H₁₈NS₂O₆ ve C₆HMePr(NO₂)(SO₃H), Formed from nitro cymene and ClSO₃H (Leone, G 11, 512) Not obtained pure —BaA" 3 aq -PbA" 4 aq needles

NITRO ISOCYMIDINE C₁₀H₁₄N₂O₂ i e C₆H₂Me(C₃H₇)(NO₂)(NH₂) Formed by heating its phthalyl derivative with conc HClAq at 180° (Kelbe a Warth, A 221, 176) Oil, volatile with

Bensoyl derivative [177°] Formed by nitrating benzoyl isocymidine (K a W) Needles (from alcohol)

Phthalyl derivative

 $C_{10}H_{12}(NO_2) \ N \ C_2O_2 \ C_6H_4$ [167°] Formed by nitrating phthalyl isocymidine Needles

NITRODECOIC ACID C, H18(NO2) CO2H product of the action of boiling HNO, on the acids of cocoanut oil (Wirz, A 104, 291)

NITRO DRACYLIC ACID IS P NITRO BENZOIC

NITRO-DULCITE v DULCITE

NITRO c-DURENE C10H13NO2 2 6

C_cHMe_c(NO₂)[1 2 3 4 5] Natro prehautene [61°] (295° 1 V) Formed by the action of HNO, on c durene (Tohl, B 21, 905) Needles Yields on reduction c duridine [70°]

Di nitro c durene $C_0Me_4(NO_2)_2$ [1 2 3 4 5 6] Formed from c durene, HNO, and H_2SO_4 in the cold (Jacobsen, B 19, 1214) and also from penta-methyl benzene and fuming HNO₃ (Gottschalk, B 20, 3287) Yellowish needles or prisms (from alcohol)

Di nitro durene $C_0Me_4(NO_2)_2$ [1 2 4 5 3 6] [205°] Formed from durene and conc HNO₃ at 0° (Fittig a Jannasch, Z 1870, 162, Nef, A 237, 3, C J 53, 428) Colourless prisms, sl sol alcohol

Di-nitro isodurene C₆Me₄(NO₂)₂ [1 2 3 5 4 6] [156°] Prepared from isodurene, HNO,, and H_2SO_4 (Jacobsen, B 15, 1853) Prisms, sl sol cold alcohol

NITRO-DURENOL C.Me. (NO2)OH Formed by nitration of durenol with ordinary HNO, at 0° Yellow crystals V e sol alcohol. nearly insol water Dissolves in alkalis with a dark-yellow colour (Jacobsen a Schnapauff, B 18, 2844)

NITRO-c DURIDINE

C_eMe₄(NO₂)(NH₂) [1 2 3 4 5 6] [131°] Formed by reducing di nitro c durene with alcoholic am monium sulphide (Töhl, B 21, 904). Red needles, sol alcohol Yields, on reduction, C₆Me₄(NH₂)₂ [140°]

NITRO-ERYTHRITE v ERYTHRITE TETRA-

NITRO ETHANE C₂H₃NO₂ * s CH₄ CH₂ NO₄. Mol w 75 (114°) S G \(\frac{1}{2}\) 10561, \(\frac{2}{3}\) 10461 (Perkin, C J 55, 689) M M 2837 S V 80 3 (Schiff, Lossen, A 254, 73) H F p 26,880 H F v 25,140 (Thomsen, Th) Formed by adding EtI to cold silver nitrite and subsequently distilling from a water bath (V Meyer, B 5, 399, A 171, 1, 175, 88, Götting, A 243, 115, Kissel, J R 1882, 226) Formed also by distilling KEtSO₄ with NaNO₂, the yield being 6 p c of the theoretical (Lauterbach, B 11, 1225), and by the action of AgNO₂ on potassium chloro propionate (Kolotoff, Bl [2] 47, 169) Oil, with pleasant odour With alcoholic sodait gives an amorphous pp of C₂H₃ONa, a salt which is very soluble in water, forming a solution in which HgCl₂ ppts crystalline C₂H₄(NO₂)HgCl The solution of sodum nitro ethane gives with FeCl₃ a blood red colour, with CuSO₄ a green solution, and with AgNO₂ a white pp rapidly turning black

Reactions —1 Iron and acetic acid reduce it to ethylamine —2 When mixed with potash and KNO, and H₂SO₄ is slowly added, there is formed ethyl introlic acid CH₂C(NOH) NO,, [81°], the alkaline salts of which form deep red solutions (V Meyer, B 7, 425) -3 Fuming H2SO4 yields ethane s di sulphonic acid -4 HClAq (SG 114) at 140° splits it up into hydroxylamine and HOAc (Meyer a Locher, A 180, 163) -5 NaOEt and EtI form only CsH, NO (168°) (Gotting) NaOMe and MeI form C, H, NO (c 155°) According to Socoloff (J R 20, 579) alcoholic soda forms C₆H₉NO (175°) and the presence of alkyl iodides does not affect the pro duct -6 ZnEt, followed by water forms di ethyl hydroxylamine and other products (Kissel, J R 1887, 109) -7 Benzoyl chloride forms di benzoyl hydroxylamine and di acetyl hydroxyl amine (Kissel, J R 1882, 40)

Constitution — The constitution of nitrotenane has been discussed by Victor Meyer (B 5,404, 8,30, A 244, 222), Geuther (B 7,1620), Alexejeff (Bl [2] 46, 266), Socoloff (Bl [2] 47, 160), Bevad (J R 20,125), and others

Di nitro methane CH, CH(NO₂)₂ (186° cor) S G ^{23.5} 1 3503 Formed by the action of KNO₂ and alcoholic potash on brome nitro ethane (Ter Meer, A 181, 1) Formed also by the action of cone HNO₂ on di ethyl ketone and on methyl acetoacetic ether (Chancel, Bl [2] 31, 504, C R 96, 1466) Oil, with sweet taste Reduced by tin and HClAq to hydroxylamine, NH₃, and HOAc Reduced by sodium amalgam to ethyl azaurolic acid —CH₃ CK(NO₂)₂ yellow monoclinic crystals, m sol cold water, insol alcohol Explodes when struck Its aqueous solution gives a reddish-brown pp with FeOl₂, a pale blue pp with CuSO₄, and a light-brown pp with HgCl₂—AgA' lustrous yellow plates

Tri - nitro - ethane (?) CH, C(NO₂), [55°]. Formed from methyl-malonic acid and HNO₈ (Franchimont, R T C 5, 281) Crystals

Tetra-nitro-ethane (?) Potasseum derevateve O.K.2(NO2). Formed from di-bromo-tetra-nitro-ethane, potash, and ammonium sulphide (Vilhers, O.R. 97, 268, 98, 431). Crystals,

which decrepitate below 100° and detonate at 200°, or even when treated with dilute acids

NITRO ETHENYL-TRI-AMIDO BENZENE C.H.,N.O., 2 e

[1 2 3 4] $C_0H_2(NO_2)(NH_2) < NH_2 > C CH_2$ [295°-

300°] Formed by heating di acetyl di nitro p-phenylene diamine with alcoholic NH_a at 150° (Nietzki a Hagenbach, B 20, 331, cf Biedermann a Ledoux, B 7, 1532) Red needles

Nitro - di - ethenyl - tetra - amido - benzene $C_{1e}H_{\nu}O_{2}N_{5}$: e

[5 1 2 3 4] C. H(NO.) (< NH > CMe). [276°] Formed by nitration of di ethenyl tetra amido-

Formed by nitration of di ethenyl tetra amidobenzene (Nietzki a Hagenbach, B 20, 331) Orange red needles (containing aq) By reduction it is reconverted into di ethenyl tetra amidobenzene —B"H₂Cl₂PtCl₄ ½aq long golden yellow needles

DI NITRO-DI-ETHENYL-TETRA AMIDO-DITOLYL

NITRO ETHENYL-PHENYLENE DIAMINE $C_eH_rN_sO_s$ so [1 8 4] $C_eH_s(NO_s) < NH > CMe$.

[216°] Formed by heating nitro o phenylene diamine with Ac₂O at 190°, cooling, and boiling with dilute H₂SO₄ (Heim, B 21, 2307) Yellowishbrown needles (from water), v sol hot alcohol

NITRO - ETHENYL - TÓLYLENE - DIAMINE $C_cH_2Me(NO_2) < N > CMe \left[1 \ 3 \ \frac{5}{4}\right]$ [246°].

Formed from acetyl p-toluidine by nitration and reduction (Bankievitch, B 21, 2402) Needles Yields on reduction ethenyl-tetra amido toluene [100°]—B"H₂Cl₂—B"HNO₃ [207°] Yellowish plates

NITRO ETHENYL-TOLYLENE-DIAMINE [185°] (L), [202°] (N) Formed by nitrating ethenyl tolylene o diamine (Ladenburg, B 8, 677, Niementowski, B 19, 723) Needles

NITRO - ETHYL - ALCOHOL $C_2H_5NO_2$ s.e $CH_2(NO_2)$ CH_2OH S G $\frac{19}{19}\frac{4}{4}$ 11691 Formed from glycol 10dhydrin and AgNO₂ (Demuth a V. Meyer, B 21, 3529, A 256, 29) Yellowish liquid, sol water, decomposed on distillation, Reacts with diazo salts yielding azo-dyes (ϵ g $C_4H_1N_2$ $CH(NO_2)$ $CH_2OH)$ Nitrous acid converts it into methyl nitrolic and glycollic acids $-CH_1(NO_4)$ CH_2ON_2 white granular powder

-CH₂(NO₂) CH₂ONa white granular powder NITRO - ETHYL - AMIDO - BENZOIC ACID C₂H₁(NO₂) 4 c [1 3 5] C₄H₂(NO₂)(NHEt) CO₂H [208°] Formed from nitro amido benzoic acid and EtBr (Rollwage, B 10, 1704) Yellow needles (from water) — BaA'₂ 4aq red needles

Nitro di-ethyl-m amido-benzoic acid $C_aH_1(NO_2)(NEt_2)CO_2H$ Monoclinic crystals; $a \ b \ c = 893 \ 1 \ 1095$ $\beta = 74^\circ \ 57'$ (Heintze, J 1886), 1454, of Lehmann, Dissert, Göttingen, 1884)

NITRO-ETHYL-AMIDO-PHENOL Netrosamene of the ethyl ether CieH13N2O4 2.6. C.H.(NO₂)(OEt) NEt(NO) Formed from C.H.(OEt) NHEt and nitrous acid (Förster, B 21, 384) Yellowish prisms Does not form

o nitro tetra ethyl-di p-amido tri-Phenyl-methane C₂₇H₃₃N₃O₂ i e

C_sH₄(NO_s) CH(C_sH,NEt_s), [110⁵] Formed by heating o-nitro benzoic aldehyde with diethylaniline and dehydrated oxalic acid (Fischer a Schmidt, B 17, 1898) Orange triclinic prisms.

p-Nitro tetra ethyl di p-amido tri-phenylmethane [113°] Obtained from p-nitro benzoic aldehyde and di ethyl aniline (Kaeswurm, B 19, 744) Thick needles or monoclinic plates

NITRO ETHYLAMINE C.H.,NH NO Ethylamine [8°] Formed from ethylamine by treatment with ClCO₂Me and decomposition of the resulting C.H.,NH CO₂Me by ammonia (Franchimont a Klobbie, R T C 7, 356)

o-NITRO ETHYL-ANILINE C.H. N.O. 16
C.H. (NO.) NHEt [1 2] Formed by heating onitro phenol with alcoholic ethylamine for
12 hours at 175° Formed also by heating the
ethylene ether of o nitro phenol with alcoholic
ethylamine at 140° (Hempel, J. pr. [2] 39, 199,
11, 162) Red oil, sol acids, but reppd by
water Yields on reduction o phenylene ethyl
diamine (249°) Nitrous acid converts it, in
ethereal solution, into di nitro ethyl aniline
[114°]

Nitrosamine C₈H₄(NO₂) NEt(NO) [30°] Formed from the hydrochloride of the base and NaNO₂ in aqueous solution Yellow needles

(from dilute alcohol or HOAc)

m.Nitro-ethyl aniline C₆H₄(NO₂)NHEt [1 3] [60°] Formed by heating m intro aniline (16 g) with EtBr (14 g) and aqueous NaOH (6 g) Formed also by adding HNO₃ (41 5 g of S G 1 39) to a cooled solution of ethyl aniline (50 g) in H₂SO₄ (1,000 g) (Nolting a Stricker, B 19, 546) Reddish yellow needles, volatile with steam With diazotised p bromo aniline it yields C₆H₄Br N₂ NEt C₆H₄NO₂ [136°] (Meldola a Streatfeild, C J 55, 429)

Nitrosamine C_eH₄(NÓ₂) NEt(NO) [47°] Acetyl derivative C_eH₄(NO₂) NEtAc

[89°]

p-Nitro ethyl-aniline C_sH_s(NO)(NHEt) [1 4] [95⁵] Obtained by intration of acetyl ethyl aniline dissolved in H₂SO_s (5 pts), the product being saponified (Weller, B 16, 31, Nölting a Collin, B 17, 267) Formed also by heating p intro aniline with EtBr and alcoholic potash at 110° (Schweitzer, B 19, 142) Yellow prisms with violet reflex (from alcohol) Somewhat volatile with steam With diazotised p-bromo aniline it yields C_sH_sBr N_s NEt C_sH_sNO_s [125⁵]

Nitrosamine C.H. (NO2) NEt(NO) [120°] Yellow needles (from alcohol) (Meldola a Streat

feild, C J 49, 61)
Acetyl der

Acetyl derivative C.H. (NO.) NEtAc

[118°]

Bensoyl derivative C.H.(NO.) NEtBz [98°] Needles, v sl sol hot water (Meldola a

Salmon, C J 53, 774)

m-Nitro-di-ethyl-aniline C_eH₄(NO₂) NEt₂[1 3] (289°) Formed, together with a small quantity of the p-isomeride, by nitration of di-ethyl-aniline dissolved in H₂SO₄ (20 pts) (Groll, B 19, 199) Obtained also by heating m-nitro-aniline (20 g) with EtI (46 g) and NaOH (12 g.)

in alcoholic solution for 8 hours at 100° (Notting a Stricker, B 19, 550) Dark yellow on

p Nitro di ethyl anline C_eH₄(NO₂) NEt₂[14] [78³] Formed by oxidation of introso di ethylanline with KMnO₄ and H₂SO₄, and also by the action of introus acid on di ethyl amido benzenezo di ethyl anline (Inppmann a Fleissner, B 16, 1422, Groll) Yellow monoclinic needles with blue reflex—B'H₂PtCl₆ thin prisms

Di nitro ethyl anline

Di nitro etayl annine $C_0H_3(NO_2)_2$ NHEt [4 2 1] [114°] Formed from bromo di nitro benzene and alcoholic ethylamine (Van Romburgh, R T C 2, 104) Formed also by boiling C_0H_3 NEtAc with dilute HNO₃ (S G 1029) (Norton a Allen, B 18, 1997), and by the action of nitrous acid on an ethereal solution of o nitro ethyl aniline (Hempel, J pr [2] 39, 199, 41, 168) Yellow needles (from alcohol) Decomposed by boiling cone KOHAq into ethyl amine and di nitro phenol

Di-nitro-di-ethyl-aniline C₈H₃(NO₂)₂NEt₂ [4 2 1] [80°] Prepared by nitrating di ethyl aniline, and also by treating bromo di nitro benzene with diethylamine (Van Romburgh, R T C 2, 35, 8, 251) Yellow needles Decomposed by boiling aqueous KOH into diethylamine and di nitro phenol When gently oxidised by CrO₃ it yields di nitro aniline [175°]

Tri-ntro-ethyl-anilne C_aH₁(NO₂), NHEt Ethylproramide [84°] Formed from chlorotri nitro benzene (pieryl chloride) and NH, Et in alcohol (Van Romburgh, R T C 2, 107) Crystals (from alcohol) which turn brown in air

Tri nitro-di-ethyl aniline C₆H₄(NO₂), NEt₂ [164°] Prepared by adding a hot alcoholic solution of NHEt₂ to (1,2,4,6) chloro-tri nitro benzene Orange crystals (from benzene) Decomposed by potash into picnic acid and diethylamine

Tetra-nitro-ethyl-aniline

C₀H₂(NO₂)₃ NEt(NO₂) Nitramine of tri nitroethyl aniline [96°] Obtained by the action of HNO₃ and H₂SO₄ on ethyl aniline and on diethyl aniline (Van Romburgh, R T C 2, 31, 114) Yellow plates (from alcohol) Decomposed by 10 pc aqueous Na₂CO₂ into pieric acid and ethylamine Reduced by tin and HClAq to tri amido phenol

NITRO-ETHYL-ANTHRONE C₁₈H₁₃NO₃ e.e. C₆H₄C₆H₄ [102°] Formed, as a by-product, in the preparation of ethyl anthracene hydride nitrite by the action of HNO₃ on ethyl anthracene hydride dissolved in HOAc (Luebermann a Landshoff, B 14, 474)

(Liebermann a Landshoff, B 14, 474)
o-NITRO-ETHYL BENZENEC, H, (NO2) C, H,
[228°] S G 12 1 126 Formed, together with
the p- isomeride, by dissolving ethyl benzene in
HNO, (Beilstein a Kuhlberg, A 156, 206, Z
[2] 5, 524) Oil

p - Nitro - ethyl - benzene $C_0H_4(NO_2)$ C_2H_3 (246°) S G 25 I 124 O1l

Nitro di-ethyl bennene C₆H₄Et₂(NO₂) (155° at 23 mm) Formed from di ethyl-benzene and fuming HNO₂ at 0° (Voswinkel, B 22, 316) Oll, boils with partial decomposition at 280°–285°

Di-nitro-tetra-ethyl-bensene C_sEt_s(NO_s), [115°]. Pale yellow prisms (Galle, B 16, 1745). Tri-nitro-di-ethyl-bensene C_sH(NO_s), Et_s. [62°]. Yellow prisms (Voswinkel, B 21, 2880).

o-NITRO-ETHYL-BENZENE SULPHONIC ACID C₅H₅NSO₅ to C₅H₅(NO₅)Et SO₅H Formed by sulphonation (Beilstein a Kuhlberg, A 156, 207) -BaA'₂ S 54 at 17 5°

p - Nitro - ethyl - benzene sulphonic acid—BaA'₂5aq S 2 61 at 17 5° Needles

NITRO-p-ETHYL-BENZOIC ACID

C₄H₃Et(NO₂) CO₂H [156°] Formed from p
ethyl benzoic acid and cold fuming HNO₃
(Aschenbrandt, B 12, 1304, A 216, 220)

Needles (from water) —NaA'2aq —CaA'₂2aq —
SrA' 4aq —BaA'₂4aq leaflets, sl sol water

p - NITRO - a ETHYL BENZOYL - ACETIC ETHER C₂H₁(NO₂) CO CHEt CO_Et [40°] Formed from C₂H₄(NO₂) CO CHNa CO_Et and EtI (Perkin a Bellenot, G J 49, 451) Plates

DI-NITRO-ETHYLENE-UREA

 ${
m CO} < N({
m NO}_2) {
m CH}_2 > {
m [210^\circ]}$ Obtained from ethylene urea and HNO, (Franchimont a Klobbie, R T C 7, 17) Prisms On boiling with water it loses ${
m CO}_2$ and forms ethylene di nitramine ${
m C}_2{
m H}_4({
m NH~NO}_2)_2$ [174°]

DI-NITRO-ETHYLIC ACID C.H. A.Q. Ethylntramine? Formed from ZnEt, and NO Prepared by passing nitric oxide into a benzene solution of ZnEt, NaEt, obtained by adding sodium (12 7 g) to cold zinc ethyl (100 g) The product is successively treated with ether, alcohol, and water, zinc is ppd by CO₂, the filtrate evaporated, and the sodium salt extracted by alcohol (Franklanda Graham, C J 37,570, cf Frankland, C J 9, 89, Zuckschwerdt, B 7, 291, A 174, 302) The free acid is unstable Its salts yield ethylamine on reduction by sodium amal gam Alcoholic potash forms ethylamine and nitric acid (Zorn, B 15, 1008)—NaC.H.N.2O.2—CaA'.23aq—BaA'.2—MgA'.2—ZnA'.2—ZnA'.2aq—CuA'.23aq flat dark blue needles (from alcohol)—AgA'—AgA'AgNO.

NITRO-o-ETHYL-PHENOL C₆H,Et(NO₂) OH (212°-215°) Formed in small quantity by the action of nitrous acid on C₆H,Et NH₂ (Suida a Plohn, Sits W [2] 81, 245)—BaA'₂sq orange

plates
Di-nitro-o-ethyl-phenol
C_cH₂Et(NO.)₂OH
Formed from o ethyl phenol and cold HNO₃ (S
a P) Heavy oil—BaA'₂ (at 100°)
Plates (from alcohol)

NITRO -p-ETHYL-ISOPROPYL-BENZENE C₆H₆EtFr NO₂ (265°) Obtained from [4 1] C₄H₆EtFr and HNO₃ (Von der Becke, B 23, 3194) DI-NITRO-(B)-ETHYL-THIOPHENE

C₄H(C₂H₃)(NO₂)₂S Formed by nitration of (\$\beta\$) ethyl thiophene by passing air charged with its vapour into furning HNO₂ (Bonz, B 18, 552) Crystalline solid With alcoholic KOH it yields a blue colouration, becoming red on longer exposure to the air, or by addition of more KOH

NITRO-O ETHYL-TOLUENE

 C_aH_a MeEt(NO₂) Oil (Claus a Pieszcek, B 19, 3087)

Di-nitro o-ethyl-toluene C₆H₂MeEt(NO₂)₂.
Oil, not solid at 0°

Di-nitro-p-ethyl-toluene [52°] Obtained, with an oily isomeride, by nitrating p ethyltoluene (Jannasch a Dieckmann, B, 7, 1513)

Tri nitro-p ethyl-toluene C.HMeEt(NÓ.); [92°] Obtained by nitration (Glinzer a. Fittig, A. 186, 308) Prisms (from alcohol)

Nitro-ethyl-p toluidine $C_sH_2Me(NO_2)$ NHEE [4 3 1] [48°] Formed from ethyl p toluidine (1 pt), H_2SO_4 (20 pts), and HNO_3 (Nölting a Stricker, B 19, 549). Flat red prisms, v sol alcohol

Nitro-ethyl-p toluidine

C.H.Me(NO.) NHEt [4 2 1] [59°] Formed by heating nitro-p toluidine with EtI (Gattermann, B 18, 1483, Niementowski, B 20, 1883) Red crystals (from alcohol), v sol ether

Acetyl derivative (245°-250° at 150 mm)
Di-nitro-ethyl-o-toluidine Nitramine
[1 3 5 6] C_oH₂Me(NO₂)₂ NEt(NO₂) [72°] Formed,
in small quantity, by the action of HNO₃ on diethyl o toluidine (Van Romburgh, R T C 3,
402) Yellow crystals (from alcohol)

Di nitro ethyl p toluidine C₂H₂Me(NO₂)₂NHEt [1 3 5 4] [126°] Formed by nitration of nitro ethyl p toluidine (Gatter mann, B 18, 1485) Orange crystals

Nitrosamine C,H_s(NO₂)₂ NEt(NO) [78°] Nitramine C₆H Me(NO₂)₂ NEt(NO₂) [116°] (R, G), [106°] (N a L) Formed from di ethyl p toluidine and fuming HNO₂ (Van Romburgh, R T C 3, 408) Formed also from C₆H₄Me(NEtAc) and dilute (10 p c) HNO₂ (Norton a Livermore, B 20, 2271) Converted by bouling NeOHAa into di mitro nerses [88°]

boiling NaOHAq into di nitro p cresol [83°]
TRI-NITRO-ETHYL-0 XYLENE

C_oMe₂Et(NO₂), [121°] Needles (from alcohol) (Fittig a Ernst, A 139, 193, Stahl, B 23, 992) Tri-nitro-ethyl-m-xylene [127°] Formed from ethyl m xylene, HNO₃, and H₂SO₄ (Stahl)

White needles, m sol alcohol
Tri-nitro s ethyl m xylene [138°] Needles,
v sl sol alcohol (Jacobsen, B 7, 1434)

Tri-nitro-ethyl-p xylene [129°] Prisms (from hot alcohol) (Jacobsen, B 19, 2516)

NITRO EUGENOL C₁₀H₁₁NO₄ te C₀H₂(C₃H₃)(NO₃)(OMe)(OH) [1 5 3 4] [44°] Formed by nutration of eugenol (Weselsky a Benedikt, M 3, 387) Triclinic crystals, sl sol water Volatile with steam

Acetyl derivative [61°] Tables
NITRO EUXANTHIC ACID v EUXANTHIO

NITEO PSEUDO-FLAVENOL v FLAVENOL.

NITRO-FLUORANTHENE v Fluoranthene p NITRO-FLUORENE C₁₃H₉NO₂ + 6

 CH_2 C_0H_4 C_0

Di nitro fluorene CH₂ C_cH₁(NO₂) [201°]
Formed by nitrating fluorene (Fittig a Schmitz, A 193, 134) Needles (from HOAo)
DI NITRO FLUORESCEIN C₂₂H₁₀(NO₂yO₄

DI NITRO FLUORESCEIN $C_{20}H_{10}(NO_2)_2O_4$ Formed from fluorescein (1 pt), H_2SO_4 (20 pts), and HNO₂ (2 pts) at 0° (Baeyer, A 183, 1) Amorphous yellow powder

Dr acetyl derivative Pale-yellow needles (from alcohol) On boiling for some minutes with dilute (15 p c) KOH it forms a blue solution

Tetra - nitro - fluorescein C₂₀H₂(NO₂)₄O₅
Formed from fluorescein (1 pt) and fuming
HNO₂ (5 pts) Colourless crystals (from HOAc)
Its alcoholic solution is yellowish red, and, on

adding an acid, becomes first reddish violet and | ibid [8] 14, 89) then colourless

NITROFORM v. TRI-NITRO-METHANE NITRO-FURFURYL-ETHYLENE

C,H₂O CH CH(NO₂) [184°] From furfuralde hyde and an alkaline solution of nitro ethane (P) Yellow prisms Nitro-furfuryl-nitro-ethylene

C₄H₂(NO₂)O CH CH(NO₂) [144°] Yellow felted needles Formed by nitration of furfuryl nitro ethylene It is oxidised by CrO₂ to nitro pyro mucic acid

Dibromide [111°], yellow prisms (Priebs, B 18, 1862

NITROGEN N (Azote) At w 14 01 Mol w 28 02 Boils at -194 4° (Olszewski, W 31, According to Sarrau (C R 94, 639, 718, 845) the critical temperature of N is -128.8° , and the critical pressure is 42 1 atmos (gas) 97247 (arr = 1) SG (liquid) 885 (water = 1) at b p (O, lc, cf Wroblewski, C R 102, 1011). SG (gas) at 3000 atmos (water = 1) 823 (Amagat, C R 107, 522) VD 14 (von Jolly, W 6, 536) SHp (equal wt of water = 1) 2368, (equal volume of air = 1) 2377 (Regnault, Acad 26, 302) C E 0036677 (von Jolly, P Jubelbd 82) S 01843 at 4°, 01751 at 62° 0152 at 12 6°, 01436 at 17 7°, 01392 at 23 7°, the absorption coefficient

the absorption coembrane
= 020346 - 00053887t + 000011156t² (Bunsen,
Gasom Methoden [2nd ed] 209) S (alcohol)
12561 at 19°, 12384 at 63°, 12241 at 112°,
12148 at 146°, 12053 at 19°, 11973 at 238°, absorption-coefficient

= 126338 - 000418t + 000006t² (Carius, A 94, *136, Bunsen, Gasom Methoden [2nd ed] 209)

Refraction-equivalent
$$\left(\frac{\mu-1}{d}\right)$$
 At w = 4 1 to 5 3 (Gladstone, Pr 18, 49) Mean value of μ for white light = 1 0003019, dispersion power

= 2086 (Croullebois, A Ch [4] 26,236, \hat{v} also

Mean value of μ for

dispersion power

Mascart, P 153, 149) M M Nv c 114, N^{III} c. 611 (Perkin, C J 55, 736) T C (air = 1) 98 (Narr, P 142, 123), 993 (Plank, Carl Rep 13, 164) H C $[N^2,O] = -17,740$, [N,O] = -21,575, $\begin{array}{lll} [N,O^3] &= -2,005, & [N^2,O^3,Aq] = -6,820, \\ [N^2,O^3,Aq] &= 29,820 & (Th 2,198), & [N^2,O^3] \\ &= -22,200, & [N^2,O^3] = -1,200, & [N^2,O^3,Aq] \end{array}$ $= -8,400, [N^2,O^5,Aq] = 28,600 (Berthelot, A Ch)$ Coefficient of compressibility 750-1,000 atmos 000407, 1000-1500 atmos 000265, 1500-2000 atmos 00017, 2000-2500 atmos 000122, 2500-3000 atmos 000091 (Amagat, CR 107,522) Transpiration coefficient (0=1) 873 (Meyer a Springmuhl, P 148,526), 885 (von Obermayer, W A B 73 [2nd part], 433) Friction coefficient at 0° = 000184 (M a S, l c), 0001659 (von O, lc) The spectrum of N varies much, there are two distinct spectra, known as the elementary line spectrum and the band-

Occurrence -In the atmosphere, forming c ths by volume In the fluid-cavities of some specimens of rock crystals (Davy, T 1822 367) In the air-bladders of fishes, and in other cavities of the bodies of animals and vegetables the gases from some fumaroles In certain wells (v L Smith, Am S [2] 12, 866) Probably in the sun (Young, Am S [3] 4, 856, Draper,

spectrum (for measurements of lines, v B A 1884 429, also Ames, P M [5] 30, 48)

Compounds of N occur in very large quantities throughout the animal, vege table, and mineral, kingdom

In 1772 Rutherford (De aere mephatico, Edinburgh, 1772) showed that the expired breath of animals contained a gas which extinguished flame, but which was not carbonic acid, as it was not absorbed by potash A little later Lavoisier proved that this gas was present in air As this gas did not support animal life, Lavoisier called it azote (à and ζωή) Chaptal afterwards gave it the name netrogen, because it was present in

Formation —1 From air, by removing CO₂ by KOHAq, moisture and NH, by cone H₂SO₄, and O by passing over red hot Cu (v Preparation, No 1) —2 By passing air through a mixture of sawdust and Fe sulphide (obtained by saturating ppd Fe₂O₃ with H₂S), and then through alkaline pyrogallate solution, and finally through cone H₂SO₄ When the process is completed, passage of H₂S re forms Fe sulphide, which may be used again -3 By burning P in an inclosed quantity of air, over water, and allowing the P2O5 formed to dissolve in the water —4 By passing air through cone NH₃Aq, and then sending the mixture of air and NH₃ over Cu heated to redness, the CuO formed is reduced by the NH₂ (Lupton, C N 33, 90) -5 Berthelot (Bl [2] 13, 314) partly covers with NH₂Aq c 200 grams pure Cu turnings in a 10-14 litre flask, closes the flask by a cork carrying a safety funnel tube, and a delivery tube which is stopped by a caoutchouc cap, and shakes from time to time The O is thus com pletely removed from the air in the flask, the N may be obtained by pouring into the flask water previously freed from O by shaking with NH3Aq and Cu, the gas should be passed through KOHAq, cone H₂SO₄, and then through CrCl₂Aq (B, Bl [3] 2, 643) - 6 By shaking FeO, H_2 , or MnO₂ H_2 , with air, the hydroxides are obtained by adding NaOHAq to conc FeSO,Aq or MnSO₄Aq, and at once stopping the ingress of air -7 By placing pyrogallic acid in a flask, adding NaOHAq, corking, and shaking for some time (v Liebig, A 77, 107) -8 By passing over Pt black a mixture of 100 vols air (from which CO, has been removed) with 42 vols H (Dumoulin, L'Institut, 1851 11) -9 By passing Clinto rather dilute NH,Aq, keeping the NH, always in large excess, 8NH, +3Cl, =6NH,Cl+N,2 (the experiment is dangerous, as NCl, may be formed and explode) -10 By warming cone NH4NOAq, or more easily cone KNO₂Aq mixed with 3 vols cone NH₄ClAq, whereby KCl and NH₄NO₂ are formed and the NH₄NO₂ is decomposed (NH₄NO₂ = 2H₂O + N₂, Corenwinder, A 72, 225) Addition of conc K2Cr2O,Aq oxidises N oxides (which are generally produced to HNO, (v Preparation, No 2) Loew (B 23, 3018) has found that a 4-5 pc solution of NH,NO, is decomposed at the ordinary temperature by Pt black, with evolutional N 11 Parative points. lution of N -11 By heating in a retort an intimate mixture of equal parts dry NH,Cl and K₂Cr₂O₇, and passing the gas through FeSO₄Aq to absorb NO which is generally formed The chief change is represented approximately thus 2NH₂Ol + K₂Or₂O₂ = 2KOl + 4H₂O + Or₂O₂ + N₃ — 12. By heating powdered (MH₂)Or₂O₃, which decomposes to Or₂O₃, H₂O, and M.—18. By adding cone NH,ClAq to a strongly alkaline cone solution of NaBrO (prepared by adding Br to cold NaOHAq), N is evolved rapidly (?3NaBrO+2NH4Cl = 3NaBr+3H2O+2HCl+N2) Solution of bleaching powder may be used, but there is danger of formation and explosion of NCl₃ = 44 By heating a mixture of NH4NO2 and MnO2 to c 200° (not over 215°) (4NH4NO2+MnO2 = Mn(NO3)2+8H2O+3N2, Gatehouse, B 10, 1007) -15 N is evolved in the reactions of several metals with HNO3, the gas evolved by the action of Zn on HNO3Aq in presence of much NH4NO3 consists of c 90 p c N, with N2O and NO (Account C. J. 28 839)

and NO (Acworth, C J 28, 839)

Preparation —1 A very slow stream of air is passed from a gasholder through U tubes containing slightly moistened KOH, to absorb CO₂, then through U tubes containing CaCl₂, to absorb H2O, and then through a long hard glass tube, containing Cu turnings, or better Cu obtained by reducing CuO in H (Carius, A 94, 126), and heated to bright redness in a furnace, the gas which issues is allowed to bubble through a solution of CrCl₂, to remove any traces of O which may remain, and is then dried by passing through CaCl₂ in several U tubes, and then over P.O. Before the air stream is started, the tube containing the Cu should be heated and a stream of H passed through it, to remove traces of CuO (this is not necessary, of course, if the Cu has been prepared by reducing CuO by H), after cooling, one end of the tube should be scaled and the other connected with a Sprengel pump, and the Cu should be heated in a vacuum for some time If this precaution is not taken, the N will contain H (von Jolly, W 6,536) The solution of CrCl₂ is prepared before use by di gesting CrCl₃Aq with scrap Zn and HClAq until a clear blue liquid is obtained, which is poured into Na acetate solution, in an atmosphere of CO2, the red pp of chromium acetate is washed with H₀ containing CO₂, and is then placed in a flask closed by a cork with entrance tube (to be attached to the N apparatus), exit tube, and a funnel though which HClAq is dropped on to the acetate, which is thereby changed to CrCl, the whole of the acetate is not dissolved. to avoid free HCl, the N apparatus is at once attached to the flask (O von der Pfordten, A 228, 112) —2 Solid NH Cl is added to an almost saturated cold solution of NaNO2, when no more NII Cl dissolves the liquid is poured into a ca pacious flask, cold cone K2Cr2O7Aq is added, about 1 pt K₂Cr₂O, for each 1 pt NaNO₂ used, and the mixture is gently warmed The K₂Cr₂O, oxidises any oxides of N to HNO₂ (v Gibbs, B 10, 1387) It is advisable to pass the N through KOHAq to absorb any traces of Cl compounds coming from impurities in the salts used (Gibbs, l.c) -8 A solution of 1 pt K₂Cr₂O₇, 1 pt NH₄NO₂, and 1 pt NaNO₂, in 3 pts water is warmed in a fair sized flask (Böttger, Jahr des phys Vereins zu Frankfort, 1876-77 24)

Properties —A tasteless, colourless, odourless gas, which does not burn, nor support combus tion, nor form a pp with CaOAq Liquid N is obtained by cooling the gas to —136° under a pressure of some hundred atmos, and then reducing pressure, not too suddenly, to not less than 50 atmos., the N does not remain liquid for more

than a few seconds Liquid N is colourless, transparent, and shows a very sharp menusous (Wroblewski a Olszewski, A Ch [6] 1, 112) According to Cailletet (A Ch [5] 5, 132), N is liquefied, for a second or two, by subjecting the gas to 200 atmos pressure at 13°, and then suddenly reducing the pressure It has not suddenly reducing the pressure It has not been solidified N is slightly lighter than air. 1 litre at the sea level, lat 45° , weighs 1 2574614 grams (von Jolly, W 6, 536) N is very slightly sol water (for S v beginning of this art) Small quantities of N are absorbed by molten pig iron, Troost a Hautefeuille, C R 76, 482, 562, 80, 909, Ledebur, C C 1873 810) Wood charcoal also absorbs N, according to R A Smith, char coal which has absorbed N and O, when exposed to the air for a time gives off O only (Pr 12, 424, cf Montmagon a de Laire, Bl [2] 11, 261) N is chemically inert, it combines slowly with O when electric sparks are sent through a mixture of the gases for some time, HNO, is formed when electrolytic gas (H_2+0) is strongly com pressed and then exploded in compressed air in presence of a little KOHAq, and also when C is burnt in a mixture of strongly compressed air and O (in presence of a little KOHAq) (Hempel, B 23, 1455) N and H combine under the influence of the electric discharge At or towards white heat N combines with B, Cr, Mg, Si, and V, probably also with Al, Fe, and Zn The compounds of N are extremely numerous and exhibit great differences of properties related chemically to P, V, As, Nb, Sb, Di, Er, Ta, and B1, these elements form Group VI Most of the oxides of N are acidic, none is basic, NH3, however, is markedly basic and alkaline

(v Nitrogen group of elements, p 571)

The influence excited on the molecular volumes of N compounds by the N atoms has not yet been measured satisfactorily (for a synopsis of data v Kopp, A 250, 1) The molecular rotatory power of N compounds varies according as the N atom is in direct union with 3 or 5 other atoms, but the exact numerical value to be assigned to Ni¹¹ and N' has not yet been finally determined (v Perkin, C J 55, 680) Neither have final values been yet determined for the atomic refractions of Ni¹¹ and N'

The atomic wt of N has been determined (1) by finding the ratio of Ag to AgNO, the tat wts of Ag and O being known (Marignac, A 59, 289, Stas, Rech 50, Nouv R 281), (2) by finding the ratio of NH₂Cl to Ag needed to ppt the Cl (M, Ic, Stas, Rech 87, Nouv R 57) Supposed allotropic form of nitrogen—By passing a succession of powerful electric sparks

Supposed allotropic form of nitrogen—By passing a succession of powerful electric sparks through N at not more than 20 mm pressure, Thomson a Threlfall (Pr 40, 329) observed a diminution in the volume of the N, at 8 mm the diminution amounted to 8 to 10 pc of the original volume, after long warming to 100° the gas attained its original volume. T a T supposed that an allotropic form of N is produced under these conditions. According to Johnson C J 39, 130), when N, obtained from KNO₂Aq and NH₄ClAq, is mixed with H, and the gases are passed over spongy Pt, NH₄ is formed, but NH₄ is not produced if the gases are passed through a hot tube before coming in contact with the spongy Pt Johnson concluded that N can exist

558 NITROGEN.

in two forms one active and the other mactive, the latter being formed by the action of heat on the former (v also Johnson's pamphlet, Elementary Nitrogen, and on the Synthesis of Ammonia [Churchill, 1885])

Experiments conducted in recent years tend to show that certain plants, notably Legiminosæ, are able to absorb N from the air and build up nitrogenous material therewith. The absorption of N seems to occur in nodules which grow on the roots of the plants. For an account of the more important experiments up to the early part of 1890 v Lawes a Gilbert, Pr 46,85, abstract in N 42,41 v also Atwater a Woods, Am 12,526, also Schloesing a Laurent, C R 111,750, abstracts in C J 60,353

Reactions and Combinations —1 Combines with oxygen to form NO2 when electric sparks are sent through the gases for some time air is strongly compressed and mixed with com pressed O and some electrolytic gas (H2+O), an open tube containing KOHAq is placed in the vessel, and a spark is passed, a considerable quantity of KNO, is found in the KOHAq (Hempel, B 23, 1455) HNO, is also formed by exploding $H_2 + O$ in air at the ordinary pressure standing over Hg (Bunsen, Gasom Methoden [2nd ed], 71) Nitrites, or HNO₂, are formed in very small quantities in certain cases of combustion in air, e g when P, H, or ether is slowly burnt (Schönbein, J pr 84, 193, 86, 129, Ber thelot, A Ch [5] 12, 440, C R 108, 543, Kolbe, A 119, 176, Zoller a Grete, B 10, 2145, Ilosva, Bl [3] 2, 734) It is doubtful whether the nitrites are produced by the oxidation of N or of NH, in the air, the experiments of L T Wright (C J 35, 42) tended to show that nitrites are not formed by burning H in air from which NH, has been carefully removed According to Thosa (Bl [3] 2, 734), nitrites are formed by passing air over Pt black heated to c 250° Loew (B 23, 1443) showed that small quantities of nitrites are produced when pure Pt black is treated with pure NaOHAq in the air Neither of these sets of experiments proves conclusively that the N, and not the NH, of the air was the source of the N of the nitrites produced Schönbein's statement that N combines with ozone has been disproved by Carius (A 174, 31) -2 N combines with hydrogen to form NH, under the influence of the electric discharge (Chabrier, C R 75, 484, Donkin, Pr 21, 281, Morren, C R 48, 482, Perrot, C R 49, 204, cf Johnson, C J 39, 130, and Wright, C J 39, 359) Ramsay a Young assert that a trace of NH, 18 formed when a mixture of moist N and H is passed through a red hot tube containing iron filings (C J 45, 93) -3 At a very high temperature N combines with boron, chromium, magnessum, and silicon, and probably also with aluminium, iron, and sinc, to form nitrides (v these elements) -4 N combines with carbon to form C2N2, when induction-sparks are passed between C poles in an atmosphere of N (Morren, C R 48, 842) Cyanides are formed when a mixture of C with oxide of an alkali, or alkaline earth, metal is heated in N, Hempel (B 23, 8890) has shown that considerable quantities of cyanides are thus formed if the reaction occurs at pressures from 10 to 60 atmospheres.

Detection of nitrie nitrogen, ie N in combination as nitrite or nitrate. One part of N existing as a nitrite or nitrate in 20,000,000 parts of water suffices to give a violet-blue colour with a drop of diphenylamine sulphate in H₂SO₄ followed by 2 o c cone H₂SO₄ and stirring (v. Warington, C J 45,644)

lowed by 2 cc conc H₂SO₄ and stirring (v. Warington, C J 45, 644)

Nitrogen, acids of The compound N₂H, known as hydrasoic acid, is described under Nitrogen, hydrides of, p 559, for the Oxyacids of natrogen, p, 567

of nitrogen v p 567
Nitrogen, boride of, v Boron nitride, vol 1.
p 527

Mitrogen, bromide of ? NBr, According to Millon (A Ch [2] 69, 75) the red, very explosive, oily, liquid formed by adding KBrAq to N chloride covered with a little water is a bromide of N

Nitrogen, chloride of NCl₃ This compound is frightfully explosive Experiments must be conducted with small quantities and with the greatest care V Meyer (B 21, 26) describes a glass case in which experiments with NCl₃ may be conducted

Preparation -1 A stick of NH4Cl is suspended in as conc HClOAq as can be obtained, an oily liquid slowly collects in a small leaden basin placed at the bottom of the vessel in which the reaction proceeds (cf Troost a Hautefeuille, $C R 69, 15\overline{2}$) —2 NH ClAq saturated at 35° is poured into a glass basin, and a glass cylinder, closed at one end by parchment, and partly filled with the same NH, ClAq, is placed upright in the liquid in the basin, a Pt plate, forming the positive pole of a battery of at least 6 to 8 Grove or Bunsen cells, is immersed in the NH₄ClAq in the cylinder, and the negative pole-also a Pt plate-is placed obliquely under the parchment which closes the lower end of the cylinder very thin layer of turpentine is spread on the surface of the NH₄ClAq in the cylinder When the current is sent through the liquid very small oily drops form at the positive pole and float to the surface, where they explode on coming into contact with the turpentine (Bottger a Kolbe, A 64, 236, Böttger, \hat{J} pr 68, 374) —3 About 30 grams pure NH₄Cl are dissolved in hot water, the solution is filtered if necessary, diluted to 13 litres, and placed in a perfectly clean leaden basin, a small leaden basin with a handle is placed in the centre of the larger basin, a fairsized, very clean flask is filled with Cl, and this flask is immersed in the NH,ClAq, so that the mouth of the flask covers the small leaden dish The apparatus is placed out of direct sunlight, in a glass case with double walls, having an open door at one end (v V Meyer, B 21, 26) The door at one end ($v \nabla Meyer$, B 21, 26) Cl is slowly absorbed by the NH, ClAq which rises in the jar, when about 1 of the Cl has disappeared, oily drops begin to be formed in the liquid, these drops increase in quantity and size, and at last sink into the small leaden dish The leaden dish is very carefully removed, and its contents are poured into a small separating funnel made of very thin glass, the NH ClAq is removed by a pipette, the greatest care being taken that the liquid does not come into contact with any kind of organic matter, the oil in the funnel is repeatedly washed in the cold water till the washings are free from Cl, and a gentle stream of air is sent through the oil to remove NITROGEN

the last traces of Cl The oil is now allowed to drop from the funnel into a very small glass vessel, where it is dried by contact with a little bit of dry CaCl₂, the oil is then poured into a little weighed tube holding about 1 cc, and The very closed by a loosely fitting stopper greatest care is required in conducting these ope rations, especially the removal of the oil from the separating funnel, as the rubbing of the glass tap against the funnel is very apt to cause explosion, when a little of the oil has been dropped into the vessel in which it is to be dried, another clean glass dish must at once be placed beneath the funnel, as explosion would occur if a trace of the oil should drop on to the table (For more details v Gattermann, B 21,751) The oil thus obtained is a mixture of chlorinated ammonias NH_{s-x}Cl_x (G, lc), the composition of portions of the oil varies To prepare pure NCl_s, after washing the oil in a separating funnel till free from Cl, and separating the water as completely as possible, Gattermann passes a fairly rapid stream of pure Cl over the oil, which is in the narrow part of the funnel, for about $\frac{1}{2}$ an hour, he then washes and dries the oil in the way described. The analysis was made by decomposing the oil by NH3Aq, when N and HCl are formed (the HCl combining with excess of NH, to form NH, Cl), and estimating Cl The process is carried out by Gattermann (lc) by dropping the little weighing tube and the stopper (which is removed from the tube) into water in a flask, closed by a cork carrying a small dropping funnel and a tube passing downwards into a beaker of water, allowing about 20 cc cone NH3Aq to flow very slowly into the flask, when the decomposition is complete (about 4 hours are required) adding the water in the beaker to the contents of the flask, and boiling for a short time, adding HNO, Aq and

AgNO, Aq, and weighing the AgCl formed Properties and Reactions—A dark yellow oil, SG c 16 (determined by finding that the oil very slowly sank in Fe₂(SO₄), Aq, SG 1578, Porret, Wilson, a Kirk, G A 47,56) Explodes when exposed to direct sunlight or the light of burning Mg Explodes at c 90°-95° when heated in a perfectly clean tube $(v \ G, lc)$, explodes on contact with wood, grease, oil, or almost any kind The explosion of NCl₃ is of organic matter frightfully violent The older observers said that explosions occurred under most curious and apparently contradictory conditions, eg contact with P, As, or Se caused explosion, but no explosion occurred by contact with C, S, gum, starch, or wax Gattermann (lc) thinks that light was the cause of many of these explosions The vapour of NCl, acts on the eyes and mucous NCl, is decomposed membrane of the nostrils by cone HClAq, giving NH,Cl and Cl, NH,Aq produces NH,Ol and N, Hg forms HgCl, and N, SO,Aq produces NH,,H,SO,, and HOl, As,O,Aq and SH,Aq also set free N

The formation of NCl, from N and Cl would be accompanied by the disappearance of much heat Deville a Hautefeuille give [N, Cl³] = -38,000 (C R 69, 152, cf Ogier, A Ch [5]

References - Dulong, G A 47, 48; Porret, Wilson, a Kirk, G A 47,56, H Davy, T 1813 1, 242, Serullas, P 17, 304, Millon, A Ch [2] 69, 75, Bineau, A Ch. [8] 15, 82; Gladstone,

C J 7, 51, Deville a Hautefeuille, C R 69. 152, Böttger a Kolbe, A 64, 236, Böttger, J pr 68, 374, Gattermann, B 21, 751

559

Nitrogen, chlorophosphide, Nitrogen, phosphochloride of, p 570
Nitrogen, chlorosulphide of, v

Nitrogen, sulphochloride of, p 571

Nitrogen, fluoride of Warren (C N 55, 289) says that a yellow oil, probably a fluoride of N, is obtained by electrolysing NH,FAq, the oil explodes by contact with a gold wire

Nitrogen, hydrides of

Three compounds of N and H have been isolated, viz ammonia, NH,, hydrazine, N,H,, and hydrazoic acid N,H Ammonia is described in vol 1 p 196, and hydrazine in vol 11 p 706 As hydrazoic acid has been isolated since the publication of vol 11 this compound is described

Hydrazoic acid N₂H N N . (Asomide.

Hydrogen nitride) This acid was discovered by Curtius in 1890 (B 23, 3023)

Formation — Ethyl benzoylglycollate reacts with N₂H₄ to form benzoyl-hydrazine and the ethyl salt of hydrazine acetic acid, thus, C_sH_sCO O CH COOEt + 2N_sH_s

= C₅H₃CO NH NH₂ + NH₂NH CH₂CO₂Et + H₂O₂By the reaction of benzoyl hydrazine with NaNO₂ and acetic acid, benzoyl azoimide is formed , thus, C₆H₃CO NH NH₂ + NOOH = $C_bH_sCO N < N + 2H_2O$ By boiling this imide with NaOH the Na salts of benzoic and hydrasoic acids are produced, thus,

acids are produced $C_cH_sCON < N + 2NaOH$ $= C_cH_sCOONa + NaN < N + H_sO.$ warming,

By adding dilute H SO, Aq and warming, hydrazoïc acıd gas ıs evolved

Preparation - Ethyl hippurate is dissolved in as small a quantity as possible of boiling alcohol, N,H, HO is added in the ratio C.H.CO NH CH. COOEt N.H. H.O., hippuryl hydrazine, C.H.CO NH CH. CO NH NH, separates on cooling The crystals are recrystallised from alcohol, and dissolved in much warm water. with addition of rather more than a molecular proportion of NaNO2, the solution is cooled to 0°, and mixed with excess of acetic acid, when lustrous tablets of a nitroso compound (probably $C_0H_3CO NH CH_2 CO N < NO NH_2$) separate,

crystals are collected by help of a filter pump, washed with cold water, and dissolved in very dilute NaOHAq This solution is gently warmed for a short time on the water bath, and is then placed in a flask connected with a condenser and furnished with a dropping funnel A flask containing AgNO,Aq is used as a receiver, dilute H,SO,Aq is allowed to drop very slowly into the boiling liquid in the flask, N,H distils over with steam, and, reacting with the AgNO, in the receiver, produces AgN, the operation is continued so long as a pp is produced in the receiver The AgN, is collected by the help of the pump, and well washed with cold water, it must not be heated above 60°, else there is danger of a severe explosion The AgN, is decomposed by boiling with dilute HClaq, the dis-

NITROGEN. 560

tillate is fractionated, and the portion which distils over in the early stages is collected separately from the rest In this way a solution of N₂H containing 27 p c N₂H is obtained repeatedly fractionating with great care, N.HAq containing over 90 pc N.H is obtained, and all water can be removed from this solution by fused CaCl₂ (Curtius a Radenhausen, J pr [2] 43, 207) The process of fractionation is often attended with explosions

Properties and Reactions -A 27 p c solution of NaH is a thickish liquid, which sinks in water, it possesses an extremely offensive odour, with NH, it gives white clouds Pure N,H is a clear. Pure NaH 18 a clear, colourless, very foully smelling, liquid at 87° It is very explosive When touched with a hot substance it explodes with violence, it also explodes when placed in a barometric vacuum The solution of N_sH corrodes the skin and causes headache and giddiness NaHAq is a strong mo nobasic acid, it dissolves Fe, Zn, Cu, Al, and Mg with rapid evolution of H, it appears to dissolve slightly Au and Ag With AgNO3 Aq and HgNO3 Aq white pps of AgN3 and HgN3 are obtained The affinity of N₃HAq is a little greater than that of acetic acid. The salts of N₃H are also very explosive, with the exception of those of the alkali and alkaline earth metals

The following salts are described by Curtius (B 28, 3032) $N(NH_{43})$, $(N_3)_2Ba$, N_3Hg , N_3Ag , salts of Cu, Fe, and Na were also prepared

In connexion with N₂H v Mendelejeff, B 23, 3464

Nitrogen, iodides of (Iodamines) explosive compounds containing N and I are obtained by rubbing I with cone NH₃Aq, by pouring an alcoholic solution of I into NH₃Aq or alcoholic NH₃, by pouring NH₃ into alcoholic I, by pouring a solution of I in aqua regia into NH3Aq or NH4ClAq, by adding bleaching powder solution (neutralised by acetic acid) to NH, IAq, by adding NH, Aq to a mixed solution of HCl and HIO, by the action of N chloride on KIAq, and by adding I and alcohol to 'white precipitate' The products of these reactions are very darkcoloured powders, which explode, more or less readily and violently, by rubbing or striking Analyses of these substances seemed to show that at least three different explosive compounds existed, viz NI₂, NH₂I, and $\hat{N}_2H_3I_3$ (= N \hat{H}_3 NI₃) For details and analyses v Serullas, P 17, 304, Millon, A Ch [2] 69, 78, Marchand, J pr 19, 1, Bineau, A Ch [3] 15, 71, Gladstone, C J 4, 84, 7, 51, Bunsen, A 84, 1, Stahlschmidt, P 119, 421, Champion a Pellet, Bl [2] 24, 447, Mallet, Am 1, 4, Guyard, A Ch [6] 1, 358 Guthrie (C J [2] 1, 239), by adding I to conc NH, NO, Aq or (NH,)_CO, Aq containing KOH, ob tained a brown black liquid, which, he said, had the composition NH₂I I (v post)
Raschig (A 230, 212) has re examined the

various methods of preparing and analysing N nodides According to B, three compounds exist, NI, NH,I, and NHI, but only NI, and NH,I

have been isolated by R

TRI-IODAMINE NI. NH₄Cl and I in the ratio NH₄Cl 6I(1 14 24) were dissolved in KIAq, and NaOHAq was added in the ratio NH,Cl 4NaOH, • 6 299 parts NaOH for each part NH Clused, the black pp which forms was collected immediately (with the help of a filter-pump) and

washed 6-8 times with cold water, as rapidly as possible, then dissolved in HClAq and analysed Raschig (lc) expresses the reaction thus,

NH,ClAq +6IAq +4NaOHAq = NI₂ + NaClAq + 8NaIAq +4H₂O NI₂ is rapidly decomposed by water to NHI₂ Mallet (Am 1, 4) obtained NI, by triturating I with a large excess of the most cone NH,Aq, keeping temperature at or below 0°, pouring off the liquid and tritura ting with more NH,Aq, repeating this several times, then agitating 2 or 3 times in a cooled flask with absolute alcohol, then with dry ether, and allowing the ether to evaporate NI, 18 a heavy, nearly black, powder According to Raschig (lc), the NI, prepared by the action of NH, Aq on I is much more explosive than the nodide formed by the action of NH ClAq and NaOHAq on I NI dissolves in KCyAq, forming ICy, KOHAq, and NH,Aq (Millon, A Ch [2] 69, 78, Rasolng, A 280, 212), KSCyAq reacts similarly, producing ICy, HI, KOH, NH, and H,SO₄ (B, lc)

DI-IODAMINE NHI. Prepared similarly to

NI, using the materials in the ratio NH, Cl 4I 3NaOH (Raschig, lc) Mallet (Am 1, 4) obtained this compound by triturating I with not very cone NH, Aq at the ordinary tem perature, washing with water till NH, could not be detected in the washings, keeping under water for three days, washing with alcohol and ether, and al lowing to dry Gladstone obtained NHI₂ by act ing on an alcoholic solution of I with NH₃ ($C\ J\ 4$, 34, 7, 51), with H2S it gave HI and NH2, with SO2Aq the products were NH2, HI, and H2SO4 Stahlschmidt obtained NHI, by adding alcoholic

NH, to an alcoholic solution of I (P 119, 421)

Mono iodamne NH, I Raschig (A 230, 212) expected to obtain this compound by the reaction of NH₄Cl and NaOH with I, using these materials in the ratio NH, Cl 2I 2NaOH, but the pp was very quickly decomposed by water to NH₂ NI₂ Millon (A Ch [2] 69, 78) gave the formula NH2I to the lodide prepared by him, and Marchand (J pr 19, 1) confirmed this com position Guyard (A Ch [6] 1, 358) describes a light-brown explosive compound, decomposed by light, exploding in contact with water, pre pared by NH₂Aq reacting with I in an iodide solution, to this compound he gives the formula NH₂I, with an ammoniacal solution of a Cu salt it forms Cu₂I₂ 2NH₂I

 $N_2H_3I_3(=NH_3NI_3)$ TRI IOD DIAMINE tained by mixing cold nearly saturated alcoholic solution of I and NH, decomposed by HClAq giving NH, and ICl in the ratio 2NH, 3ICl This compound seems to have been obtained by Raschig (A 230, 212) by mixing NH, ClAq, I, and NaOHAq in the ratio NH, Cl 2I 2NaOH, and washing the

pp with water

OTHER COMPOUNDS OF NITEOGEN, IODINE, and DROGEN (1) Iodammonrum rodude, NH, II. HYDROGEN a mobile brownish red liquid, formed by adding finely powdered I to saturated NH, NO, Aq or $(NH_d)_2 CO_2 Aq$ mixed with about $\frac{1}{2}$ of an equivalent of KOH (Guthrie, C J [2] 1, 239) Soluble alcohol, ether, $CHCl_a$, CS_2 , and KIAq, decomposes by heat, giving I and probably NH, I, decomposes in the air to NH, and I, water forms NH4I, HI, and NHI, which explodes producing N, I, and H₂O According to Seamon (C N 44, 188), this compound is formed by actNITROGEN 561

ing on dry I with dry NH, and absorbing the excess of NH, by standing near H2SO4 Š describes the compound as a nearly black liquid, S G. 2 46 at 15°, solidifying at -2°, decomposing

slowly at 15°, quickly at 70°

(2) Compounds of ammonia with rodins NH, I, obtained by the action of NH, on I at 10° (Millon, A Ch [2] 69, 78), formed at 80° according to Raschig (A 241, 253) β (NH₂)₃I formed at 20° (Bineau, A Ch [3] 15, 71, Raschig, lc) γ (NH₄),I, formed at 0° δ (NH₄),I, formed at -10° (R, lc) It is doubtful whether

these bodies are true compounds or not Nitrogen, oxides of N forms five oxides N2O, NO, N2O, NO2, N2O, N2O, and N2O, are the anhydrides of HNO, and HNO, respectively, NO, reacts with water to produce both HNO and HNO, NO is obtained by the decomposition of HNOAq, but the acid has not been obtained from the oxide, NO is a neutral oxide Whether N₂O₃ exists in the gaseous state is not yet finally settled, the other oxides, with the exception of N₂O₅, are gases under ordinary conditions NO2 exhibits polymerism, at low temperature the molecular weight corresponds with the formula N₂O₄, and at higher temperatures with the formula NO₂ Besides these five oxides, there is said to exist a permitric oxide NO, or

NITROUS OXIDE N2O (Nitrogen monoxide Laughing gas) Mol w 43 98 Melts at -99°, and boils at -92° (Wills, C J [2] 12, 21) S G 1 527 S G liquid N₂O 9756 at -5°, 937 at 0°, 8964 at 10°, 8365 at 20° (Andréeff, A Ch [3] 56, 317, cf Wills, C N 28, 170, Wroblewski, C R 97, 166, Cailletet a Mathias, C R 102, V D 22 1 SHp (equal wt of H.O=1) 16° to 207° = 22616 (Regnault, Acad 26, 1), 26° to $103^{\circ} = 2126$, 27° to $206^{\circ} = 2241$ (Wiedemann,

SHp 1 3106 at 0°, 1 27238 at P M [5] 2, 81)

100° (Clausius, Mechan Warmetheorie, 1 62) C E (22° to 98°) 0037067 (von Jolly, P Jubelbd 82) S 1 305 at 0°, 1 095 at 5°, 92 at 10°, 778 at 15°, 67 at 20°, absorption coefficient = 1 30521 - 045362t + 0006843t (Carius, A - 045362t + 0006843t (Carius, A Absorption coefficient in alcohol 94, 139) = $4\ 17805 - 069816t + 000609t$ (Carus, lc) H F [N, O] = -17,740, [NO, N] = 3835 (Th 2 198) For vapour pressures from -25° to 40° v Regnault, J 1863 66

Nitrous oxide was discovered by Priestley in

1776, and carefully studied by Davy

Formation —1 By dissolving Zn in HNO,Aq (SG 12 diluted with an equal vol of water) 2 By decomposition of NH₂OHAq by AgNO₃, K₂C₄O₄, &c. v Hydroxylamine, Reactions, No 1 (vol ii p 735) -3 By the gradual decomposition of H₂N₂O₂Aq (v Hyponitrous acid, p 569) — 4 By the action of SnCl₂ in HCl on HNO₂Aq or a nitrate -5 By passing NO through SO₂Aq or an acid sulphite -6 By the action of HNO, Aq on Cu in presence of much Cu2NO, if NH, NO, is present, much N2O and N, with little NO, are produced (Acworth, C J 28, 828)

Preparation -1 Pure NH, NO, is slowly heated in a retort to a temperature at which gas begins to be given off The gas flame is then lowered, and the decomposition allowed to proceed NH, NO, = N2O + 2H2O It is best to make the (explosions occur with H) -6. Easily burnt sub Vor III

NH, NO, by neutralising pure dilute HNO, Aq with pure NH,Aq or (NH,)2CO,Aq, evaporating till the BP gets to c 120° and a drop solidifies on a cold plate, allowing to cool, and breaking up into small pieces. If the temperature rises above 250°, decomposition to N, O, and H₂O may occur with explosive violence, in the change $NH_4NO_1 = N_2O + 2H_2Oc$ 31,100 cals are produced, whereas the change $NH_1NO_2 = N_2 + O + 2H_2O$ is accompanied by the production of c 48,700 cals (Th 2, 205) To obviate explosions, Case cals $(Th^2, 205)$ To obviate explosions, Case neuve (D P J 257, 435) recommends to dry NH, NO, carefully over a low flame, to bring the salt while warm into a retort or flask, to heat with a very small flame which is gradually increased till decomposition begins, and then to withdraw the flame The gas is collected over hot water, brine, or Hg If the gas is to be used as an anæsthetic, the greatest care should be taken that the NH, NO, used is pure, and especially that it is quite free from NH,Cl, else the N₂O may contain Cl, the gas should be passed through KOHAq and FeSO₄Aq to absorb traces of Cl, NO, and NO -2 A mixture of 5 parts SnCl₂, 10 parts HClAq SG 121, and 9 parts HNO, Aq SG 138, is heated to boiling, when pure NoO is evolved in a regular stream, any alteration in the proportions may cause explo sions (Campari, \hat{C} \hat{C} 1888 1569)

Properties -A colourless gas, with a slightly sweetish smell and taste Supports combustion almost as well as O When breathed, N₂O pro duces insensibility, which lasts for a short time only It is often used as an anæsthetic in dental operations, for this purpose it is usually much compressed in iron bottles N.O is decomposed by heat, the decomposition being complete at c 900° H and N20 forms an expressive mixture, most inflammable gases burn in NO N₂O 18 liquefied at 0° by a pressure of c 30° atmos, the liquid occupies c $\frac{1}{30}$ of the volume of the gas (Faraday, A 56, 157) Liquid N O is colourless and very mobile, a drop burns when let fall on the skin, on evaporation much cold is produced, liquid N₂O boils in liquid CO₂ Metals dropped into liquid N2O generally hiss as hot iron does in water Glowing C swims on the liquid and burns briskly do not react Water freezes when added to liquid N2O, but so sudden an evolution of vapour occurs that an explosion generally takes place (Faraday, A 56, 157), nitric and sulphuric acids are frozen by liquid N₂O, alcohol, ether, and CS, mix, without freezing By evaporating and CS, mix, without freezing By evaporating liquid N_2O in an air stream, Wills (C J [2] 12, 21) obtained solid NO in some quantity, the solid is a snow like substance, more compact than solid CO, when slightly warmed it melts, at c -99° , and then boils, at c -92°

Reactions —1 Decomposed by heat to N and O, change is complete at c 900° (Langer a V Meyer, Pyrochemische Untersuchungen [Bruns wick, 1885], 65, cf Berthelot, C R 77, 1448) — 2 Decomposed to N and O, by electric sparks 3 Passed over red-hot iron, Fe O, and N are formed -4 Potassium or sodium burns in N2O setting free N-5 Mixed with hydrogen, or other combustible gas such as CO, PH, H2S, or a hydrocarbon, and brought to a flame, combustion ensues at the expense of the O of the N O

NITROGEN 562

stances, when inflamed and plunged into N2O, burn almost as rapidly as in O, eg C, P, S, Na, &c -7 Mixed with oxygen, and subjected to the electric discharge, NO2 is formed -8 A solution of N₂O in water is neutral to litmus, N₂O is, however, related to the acid H2N2O2, as it is obtained by the decomposition of this acid in aqueous solution (v $\bar{H}yponitrous$ acid, p 569) The hyponitrites may be regarded as compounds of the negative radicle N₂O with more positive

oxides, e g Ag₂O N₂O
References to older memours—Gay Lussac, G A 58, 29, W Henry, Annals of Phil 24, 299, 344, Pleischl, S 38, 461, Davy, G A 6, 105, Natterer, P 62,133, Dumas, C R 27, 463

NITRIC OXIDE NO (Nitrogen dioxide Deutoxide of nitrogen Nitrous gas or arr)
Mol w 29 97 VD 15, not changed from
-100° to 1200° (Daccomo a V Meyer, B 20,
1832, Langer a Meyer, Pyrometrische Unter
suchungen [1885] 66) S H p (equal wt of H₂O =1) 13° to 172° = 23173 (Regnault, Acad 26, 1), SHv (equal wt of H₂O=1) 1652 (Clausius, Mechan Wärmetheorie, 1, 62) S c 05 at ordi mary temp S (in alcohol) 309 at 2°, 282 at 118°, 266 at 20° (Bunsen, Gasom Methoden, [2nd ed] 227) S (in H_2SO_4 S G 184) at 13° = 35, S (in H_2SO_4 A G G 15) at 18° =17 (Lunge, B 18, 1391) H F [N, O] = -21,575, [N'O,O] = -25,410

NO is liquefied at the following temperatures and pressures (Olszewski, C R 100, 940)

Pressure in atmos 71 2 578 499 -935°-975°-1009°-105° Temperature 20 Pressure in atmos 316 106 -110 9° -119° -129° -138° Temperature 1 atmo 138 mm -153 6° -167° Pressure 18 mm -1765° Temperature

The critical temp is c -935° according to Olszewski, but according to Cailletet (C R 85, 1016) NO is liquefied at -11° under a pressure of 104 atmos, but not at 8° even under 270 atmos pressure NO solidifies at -167° (Olszewski,

NO was discovered by Priestley and called

by him saltpetre gas

Formation -1 NO is probably formed in the first stages of those combustions in air whereby nitrites and nitrates are produced, e g in burning air with compressed O, in slowly burning P, ether, &c, in air (v Nitrogen, Reactions, No 1, p 558) NO is also probably formed when electric sparks are passed through a mixture of N and O —2 By reducing HNO_sAq or HNO2Aq, eg by reaction with Cu, by passing in SO2, by electrolysis, &c (v Nitric Acid, Reactions, Nos 3, 4, 5, p 520) -8 By reacting on KNO, with FeCl2Aq and HClAq, or with FeSO, Aq and H2SO4Aq

Preparation -1 A quantity of HClAq 18 divided into 2 equal parts, one portion is converted into FeCl2Aq by dissolving iron wire in it until it is saturated, the two portions are then mixed and placed in a retort or flask, KNO. is added in quantity nearly equal to that of the Fe used, and the whole is warmed (6FeCl₂Aq + 8HClAq + 2KNO₂

= 6Fe \tilde{C} l, \tilde{A} q + 2KCl \tilde{A} q + 4H, \tilde{O} + 2NO). Fe SO_4 \tilde{A} q and H₂SO₂Aq may be substituted for FeCl.Aq

and HClAq -2 Cu cuttings are added to HNO, Aq, SG 12, in a flask arranged so that it can be surrounded by cold water when desired, action begins after a little and red fumes of NO2 are evolved, when the gas in the flask is quite colourless it is collected over cold water, or if required dry it is passed over solid dry KOH and then through conc H2SO, About 130 cc acid are used for 15 grams Cu The HNO3Aq used should not be more conc than SG 12, and temperature must be kept as low as possible, else N₂O and N₂O₃ may be formed If the action proceeds for some time the gas contains con siderable quantities of N₂O, as the reaction of Cu with much Cu(NO₃)₂Aq in presence of HNO₃ produces this gas (Acworth, C J 28, 828) But with all precautions, NO prepared by this method is always liable to contain N₂O and N (v Ac worth, lc) Carius (A 94, 138) says NO can be obtained pure by passing the products of the reaction of Cu with HNO, Aq into FeSO, Aq, which absorbs NO but not N₂O or N, and then gently warming the solution thus obtained -3 Kammerer (B 18, 3064) recommends to fill a Wolff's bottle with Cu turnings, add enough cold saturated NaNO Aq to fill the bottle 1, and then allow cone H₂SO₄ to drop in little by little—4 Thiele (A 253, 246) prepares NO by adding cone NaNO₂Aq (free from carbonate) to FeCl₂ or FeSO₄ in HClAq -5 SO₂ is prepared by heating Cu with cone H₂SO₄, and passed into slightly warmed HNO3Aq SG 115, the issuing gas is passed through wash bottles wherein excess of SO, is absorbed $(3SO_2 + 2HNO_3Aq + 2H_2O = 3H_2SO_4Aq + 2NO)$

Properties - A colourless gas, at great pres sure and very low temperature, a colourless liquid, becomes solid at -167° As NO com bines with O immediately on coming into con tact with air, it cannot be determined whether pure NO is or is not tasteless and odourless Sl sol water, v sl sol H2SO4, less sol H2SO4Aq NO does not change the colour of litmus Sub stances which produce much heat when burning, eg P and C, continue to burn in NO if plunged into the gas when burning vigorously, burning S or H, or a burning taper, ceases to burn in NO A mixture of NO and H is not explosive NO is reduced to N2O by Zn, Fe, SO2, &c At a very high temperature, c 1700°, NO is decomposed

to N and O

The SG of NO has been determined from -100° to 1200° (v beginning of this article), for this temperature interval the molecular formula 18 NO

NO is a neutral oxide In the compound NOCI, formed by the union of NO and Cl, NO acts as the more positive radicle, it also per haps takes the part of the positive radicle in nitrosulphuric acid, which may be regarded as SO2OH ONO

Reactions -1 Decomposed into N and O by heat, but only at a very high temperature, c 1700°, according to Langer and V Meyer (Pyrochemische Untersuchungen, 66) -2 Elec tric sparks produce N.O (which then goes to N and O) and O (Berthelot, Bl [2] 26, 101) — 8 Reduced to N₂O by many easily oxidised substances, eg moist sinc or iron filings (NH, also is produced), sulphur droxide and water (reductions occurs even in presence of O if H.SO, is also present, v Lunge, C J 47, 465), hot copper, &c —4 Heated with potassium or sodium, K.O or Na₂O and N are formed —5 Passed over red hot carpon N and CO₂ are obtained —6 Mixed with hydrogen and inflamed, H2O and N are formed NH, is formed by passing a mixture of NO and H over spongy Pt (L Wright, C J 89, 357) — 7 The copper-sinc couple acting on NO in presence of water produces NH₂ (Gladstone a Tribe, O J 43, 341) -8 Stannous chloride, in presence of HClAq, produces NH2OH HCl, N, and SnCl., the action ceases at 100° (Divers a Haga, C J 47, 623) -9 When a flame is brought to a mixture of NO and carbon disulphide, CO2, SO2, and N are produced very rapidly, and with a brilliant white flash -10 In rapidly, and with a brilliant white flash — 10 In contact with water in the dark slowly produces HNO₂Aq, N, and a little N₂O (Cooke, C N 58, 115, cf Russell a Lapraik, C J 32, 37) — 11 Contact with cone potash solution causes a slow formation of KNO₂Aq, N₂O, and N (Gay-Lussac, Gm 2, 378, Russell a Lapraik, C J 32, 35) — 12 With alkaline solution of pyrogallol N₂O and N are formed (R a L, l c) — 28 Reduced to NH, with separation of L by 18 Reduced to NH₃, with separation of I, by cone hydriodic acid solution (Chapman, C J [2] 5, 166) —14 An alkaline solution of stannous hydroxide (= K_2SnO_2) produces $K_2N_2O_2$ and K_2SnO_3 (Divers a Haga, C J 47, 361) —15 Ferrous hydroxide, in presence of much conc KOHAq, reduces N_2O to NH_3 (D a H, l c) — 16 Oxidised to HNO, Aq by an alkaline solution of potassium permanganate, with separation of MnO₂xH₂O (Wanklyn a Cooper, P M [5] 6, 288) -17 Oxidised to NO₂ and N₂O₃ by nitric acid of S G > 115-18 With nitric acid in sulphuric acid, SO2 OH ONO is produced -With oxygen and water NO is wholly oxidised to HNO, Aq (Lunge, C J 47, 465) 20 With oxygen and conc sulphuric acid forms

SO₂OH ONO (L, lc)

Combinations —1 With oxygen to form NO₂. According to Lunge (C J 47, 465), NO, is the chief or only product when excess of O is used, but with excess of NO both NO2 and N2O3 are formed -2 With ferrous salts in solution, to form deep brown coloured liquids Gay (A Ch [6], 5, 145) finds that the quantity of NO ab sorbed is independent of the kind of ferrous salt used and of dilution It is proportional to the quantity of Fe in solution, and varies with temperature and pressure The relation between quantity of NO absorbed and pressure is a special one, it resembles that which holds good in the solution of NH, by water solutions lose all NO in vacuo, or by passing a stream of H into them The quantity of NO absorbed at 8° and 760 mm nearly agrees with absorbed at 6° and 700 mm nearly agrees with the formula 2NO 3FeSO₄, between 8° and nearly 25° the formula NO 2FeSO₄ approximately expresses the quantity of NO absorbed, and at c 25° the NO agrees with that required by NO 5FeSO₄ NO is also absorbed by chromous, stannous, and mercurous salt solutions -3 With antimony chloride, to form NO 2SbCla, also with aluminium, bismuth, and ferric chloride (Beeson, C R 108, 1012) —4 NO combines with liquid

N₂O₄ to form N₂O₃ (q v)

References to older memows—Gay-Lussac,

A Oh [3] 28, 229, Millon, C. R 14, 908,
Carius, A 94, 188

NITROGEN TRIOXIDE N₂O₃. (Nitrous anhydride Nitrogen sesquioxide) Mol w 75 9 (v. infra)

Formation —1 By passing NO into liquid N₂O₄ at c 20°, more or less pure liquid N₂O₅ is formed (Dulong, A. Ch. 2, 317, Péligot, A. 39, 327, Ramsay, C. J. 57, 590). According to Hasenbach (J. pr. [2] 4, 1), N₂O₃ is produced by passing a mixture of NO and NO₂ through a hot tube, and then into a vessel surrounded by a freezing mixture Ramsay a Cundall (C J 47, 672) showed that no contraction occurs when NO. and NO are mixed at the ordinary temperature -2 By reacting on starch or As₂O₃ with HNO₃Aq S G 1 3 to 1 35 (Lunge, B 11, 1641, Stenhouse a Groves, C J 31, 545) -3 Fritzsche (J pr 22, 14) gently warmed red fuming HNO3, condensed the vapour, again very gently warmed this liquid, and passed the vapour into a strongly cooled receiver, to 92 parts of the liquid thus obtained (chiefly N₂O₄) he added 45 parts of cold water very slowly, the liquid being kept very Two la, ers of liquid were thus obtained the under was very deep blue, and was regarded by Fritzsche as fairly pure N2O3, the upper layer, which was grass green, was a solution of N₂O₃ and NO₂ in HNO₃Aq By placing both liquids in a retort kept at 0°, the lower layer boiled, and a pure indigo blue liquid condensed in the very strongly cooled receiver, this liquid consists chiefly of N2O3 according to Intzsche F (lc) obtained a deep blue liquid, containing, according to him, at least 93 4 p c N2O2, by distilling a large quantity of nitric acid which had been used in a battery, condensing the distillate in a vessel surrounded by snow and CaCl₂, and redistilling several times at the lowest possible temperature -4 By the reaction of O on excess of NO, considerable quantities of N_2O_3 are produced (Lunge, C J 47, 466) —5 By dropping water on to 'chamber crystals' (nitrosyl sulphate, SO. OH ONO) (Streiff, B 5, 285)

Preparation —Pure N₂O₃ has not been obtained 1 The gas obtained by reacting on starch or powdered As₂O₃ with HNO₃Aq S G 1 35 is nearly pure N₂O₃, according to Lunge (B 11, 1229, 1641), the starch is made into a paste with water, and the acid is added from a dropping funnel, the flask is gently warmed, and then plunged into cold water Stenhouse a. Groves (C J 31, 545) also recommend HNO₃Aq S G, the reaction proceeds at 70° with production of nearly pure N O₃ —2 Pure NO is passed into cold liquid N O₄. The product is not pure N₂O₄ (Ramsay, C J 57, 591) But v Lunge, Z anorg, Chem 7, 209 [1894]

Properties — The liquid obtained by con-

Properties — The liquid obtained by condensing the gaseous product of the reaction between As, O, and HNO, Aq, SG 13, at 70°, passing the vapour of this liquid over P,O,, and condensing again, is deep blue, it does not solidify at -90°, it is miscible with liquid N,O, O passed into liquid N,O, mixed with N,O, very slowly, if at all, combines with the N,O, very slowly, if at all, combines with the N,O, liquid N,O, appears to dissociate slightly to NO and N,O, at -90° (Ramsay, C J 57, 597) Gaines (C N 48, 97) says that N,O, liquefies at -14 4° According to Geuther, liquid N,O, boils at 35°, and has the following SG 1464 at -8°, 14555 at -4°, 1451 at -1°, 1449 at 0°, 14485 at 1°, 1447 at 2° Birhaus

(C~R~109,68) says that N_2O_3 solidifies at -82° , Ramsay found the blue liquid to remain liquid at -90° (Birhaus's liquid probably contained N_2O_4 , as it was formed by the action of O on

excess of NO2)

Molecular weight of nitrogen trioxide -Ramsay determined the lowering of the freezing-point of N₂O₄, after passing in NO and calculating the quantity of N2O3 produced by the increase in weight, his results, on the whole, are in favour of the formula N₂O₃ for the liquid compound There has been much discussion as to the existence of this oxide in the state of gas Some chemists deny the existence of a compound nN2O2, and say that the reactions of this supposed compound are those of a mixture of NO and NO₂ (containing variable quantities of N₂O₄ according to the temperature) As NO rapidly combines with O, a mixture of NO and NO. would also surely combine with O, but Ramsay a Cundall have shown $(C \ J \ 47, \ 187)$ that Oacts very slowly on the blue liquid which, on the hypothesis of the non existence of N₂O₃, is a mixture of NO and N2O4, this result is confirmed by Ramsay's later observations (C J 57, 597), and also by observations made by Richardson (C J51, 397) Lunge has shown (D P J 233, 63) that the gas from the blue liquid which has the empirical composition N₂O₃ is not wholly transformed into NO2 even in presence of 10 times as much O as is required on the assumption that the gas in question is a mixture of NO and Moreover, Ramsay a Cundall (C J 47, 672) showed that although no change in appearance or volume occurs when NO2 gas is mixed with NO, yet on lowering the temperature of the mixed gases, by HClAq and ice, a dark blue liquid was formed (liquid NO is colourless, and liquid N₂O₄ is yellow red) Again, Ramsay (C J. 57, 597) found that the blue liquid does not freeze at -90°, but part of a mixture of NO and N_2O_4 would freeze at -10° , as this is about the freezing point of N_2O_4 . Some of the reactions of N_2O_8 with alkalis, H_2SO_4 , &c, are scarcely those of a mixture of two substances (v Reactions, 1, 2, and 5) According to Gay Lussac (G A 58, 29) a mixture of excess of NO with O allowed to stand for a long time over KOHAq forms KNO₂Aq, and the gases disappear in the ratio required to form N O₃

As regards the existence of N2O3 as a gas, Lunge's experiments show that the oxidation of the gas obtained by heating starch with HNO, Aq S G 1 35 to NO₂ is not completed by a very large excess of O (D \dot{P} J 233,63, B 12,857) Now, as Lunge has also shown (C J 47,465), that NO 11s the sole product, or almost the sole product, of the action of excess of O on NO, and therefore as soon as O is added to NO there must be present a mixture of NO, NO2, and O, it is difficult to escape the conclusion that the action of a large excess of O on a mixture of NO and NO2 must result in the formation of much NO2, and that, thererore, the gas obtained by HNO, Aq acting on starch, contains N₂O₃, which is not oxidised by O to N.O. Ramsay a Cundall (C J 47, 672) found that no contraction occurred on mixing NO2 with NO, if any N2O2 were formed contraction must have occurred R a C prepared a blue liquid having the composition N₂O₂ (by action of HNO₂Aq on As₂O₂), and determined the

VD of the gas obtained by gently warming the reponding to N_2O_3 = 38 If the gas was supposed to be a mixture of NO, NO₂, and N_2O_3 (without any N_2O_4), there must have been present 17 63 pc N_2O_3 to raise the S G of NO + NO₂ to 22 35, hence the maximum percentage of N2O3 gas which could be present was 1768, but as the gas certainly contained some N₂O₄, the percentage of N₂O₂ gas must have been less than 17 63 R a C show that a mixture of NO, NO₂, and N₁O₄, having the same percentage of N and O as N₂O₃, would have the V D 23 42 under the conditions of their experiment, assum ing a formula given by Willard Gibbs to be cor rect, hence they conclude that the gas examined by them was more probably a mixture of NO, NO₂, and N₂O₄, than a mixture of these gases with N₂O₃ R a C also draw attention to the remarkable result of Lunge's experiments, which he has himself stated, that the dissociation of N₂O₃ (supposing it to exist as a gas) is almost independent of temperature According to Luck (Fr 8, 402) and Moser (W 2, 139), the absorp tion-spectrum of the gas supposed to be $N_{2}O_{3}$ is identical with that of NO_{2} (containing $N_{2}O_{4}$) On the question of the existence or non exist ence of gaseous NO₃, besides the memoirs referred to, v Lunge, B 11, 1232, 1641, 12, 357, 15, 495, Witt, B 12, 2188, Geuther, A 245,

Reactions -1 Dissolves in water at 0°. forming a blue liquid, on warming, NO is evolved and HNO, Aq remains, if the solution is neutralised by alkali, a mixture of a nitrite (MNO₂) and nitrate (MNO₃) is obtained Ac cording to Fremy (C R 79, 61) addition of a little water causes evolution of pure NO, and HNO₃ is formed, but addition of much cold water produces a fairly stable solution, which may be kept unchanged for some days, and which slowly evolves NO and N₂O₄ on warming Addition of sand, powdered CaSO₄, or other indifferent substance, causes rapid decomposition to HNO, Aq and NO The solution is a strong reducer, cold SO₂Aq forms various nitro derivatives of S oxy acids, warm SO₂Aq forms NO, N, NH₃, and H₂SO₄ (F, lc, cf Reinsch, J pr 28, 399) —2 Passed into alkali solution, nitrite and nitrate are formed (cf Nitrous acid and Nitrites, p 567) Gay Lussac (G A 58, 29) says that KNO_2 is formed by allowing O, mixed with a large excess of NO, to stand over KOHAq, and that the gases disappear in the ratio required to form N₂O₃ —3 Decomposes urea evolving N —4 With benzenoid primary amido compounds, forms diazo- compounds (q v vol 1 p 397) With paraffinoid amido compounds, the general result is to substitute OH for NH₂ and evolve N -5 With conc sulphuric acid, nitrosyl sulphate (SO₂ OH ONO) is formed As NO₂ reacts with cone H₂SO₄ to form SO₂ OH ONO and HNO₃, and as NO passed into H₂SO₄ containing HNO₃ forms SO₂ OH ONO and H₂O, it is sometimes argued that the reaction of N₂O₄ with H₂SO₄ is easily explained by the view that regards N₂O₄ as a mixture of NO and NO2, if this view is held, then the two reactions

(1) 2NO₂+H₂SO₄ = SO₂ OH ONO + HNO₃; (2) HNO₃+2NO+8H₂SO₄ NITROGEN 565

= 3SO₂ OH ONO + 2H₂O must proceed simultaneously and at equal rates, and the supposed mixture must never contain more NO than is shown by the ratio NO NO₂, otherwise some NO would pass on unabsorbed According to Lunge (1c) (confirmed by Groves, G S Proc 1, 24), NO only slowly converts H₂SO₄ containing HNO₂ into SO₂ OH ONO

Combinations —According to Weber (P 118, 471) N₂O₂ combines with SnCl₄ and TiCl₄, e g to form SnCl₄ N₂O₂

NITEOGEN DIOXIDE NO,, and TETROXIDE O. (Nitrogen peroxide Nitroso nitric an-N₂O₄ (Nitrogen peroxide hydride) The mol w of the compound NnO2n varies with temperature, at low temperatures and small pressure (c -12° at 115 mm) the mol w is 91 86 = N₂O₄, and at moderately high temperatures (c 150°) the mol w is $45\,93 = \mathrm{NO_2}$ (v infra) N₂O, melts at -10° (Deville a Troost, C R 64, 257, Ramsay, C J 57, 590) Boils at 21 64° (760 mm, Thorpe, C J 87, 224) 8 G $(\text{liquid})_{70}^{00} = 14903 \text{ (Thorpe, } lc)$ V.D at -12° and 1154 mm = 4254 (Natanson, W 27, 606), at 130° a 718 mm = 23 26 (Richardson, C J 51, 397), at 183° a 760 mm = 22 7 (Deville a Troost, C R 64, 237), at 27° a 16 to 35 mm = 23 1 (Troost, C R 86, 1395) SH (liquid) 46 (Ramsay, C J 57, 590), for SH at different temperature of the state of ratures v Berthelot a Ogier (A Ch [5] 30, 382) For heat of fusion v Ramsay (lc) H F [N,0] For heat of fusion v Ramsay (lc) H F [N,0'] = -2,005, [NO,0] = 19,570, [N,0',Aq] = 5,750 (Th 2, 199) For electrical resistance of liquid N₂O₄ v Boguski (Z P C 5, 69) For absorption-spectrum v Kundt (P 141, 157), Gernez (C R 74, 465), Luck (Z [2] 6, 287) For thermal expansion v Thorpe (C J 37, 224)

Molecular weights of introgen peroxide — The VD at low temperatures near the liquefying point corresponds with the formula N₂O₄, and the same formula expresses the molecular composition at c 27° under a pressure of 16 to 35 mm, when heated to c 150° the VD shows that the molecular formula is NO₂. Measurements of VD are given by Deville a Troost (C R 64, 257), Troost (C R 86, 1395), Playfair a Wanklyn (C J 15, 156), E a L Natanson (W 27, 606), Richardson (C J 51, 397) That the change in VD measures a process of dissociation from N₂O₄ to NO₂ has been shown by Natanson (Ic), Naumann (A Suppl 6, 205, B 11, 2045), Salet (C R 67, 488) The amount of dissociation is increased by raising temperature or lowering pressure (v especially Natanson, Lc) Ramsay determined the lowering of the freezing point of acetic acid by dissolving N peroxide in it (C J 53, 621), and also the lowering of f p of C₂H₂Cl and CHOl₂ by the peroxide (C J 57, 990), both results tend to show that the mol w of the liquid compound is N₂O₄

Formation—1 By passing electric sparks through a mixture of O and N—2 By bringing NO into contact with excess of air or O—3 By heating Ph(NO₃)_x.—4 By the action of AgNO₂+NO₂Cl (Exner, C C 1872 278), but the existence of NO₂Cl is denied by Williams (C. J. 49, 226).—5 According to Hasenbach (J pr [2] 4, 1), by passing O into the liquid obtained by heating starch with HNO₂Aq and condensing, but the observations of Ramsay a Cundall (C J 47, 187) show that O very slowly, if at all, combines

with N₂O₃ —6 By the reaction between NOCl and KNO₃ (Girard a Pabst, Bl [2] 30, 351)

Preparation —1 A mixture of dry NO and about an equal volume of dry O is passed over dry KOH, and then into a vessel cooled to —20°, solid N₂O₄ is thus obtained (Péligot, A 9, 259, 39, 327, cf Dulong, G A 58, 53, a Lunge, C J 47, 465)—2 Dry powdered Pb(NO₃)₂ is heated in a tube of hard glass, and the gas is passed into a U tube cooled to c—8°, a stream of dry O is passed through the liquid in the U tube for some time (Péligot, Ic, Thorpe, C J 37, 224)—3 By very gently heating As₂O₃ with HNO₃Aq S G 15 and a little cone H₂SO₄, and passing O into the liquid thus obtained (cf Ramsay a Cundall, C J 47, 187, with Lunge, B 11, 1641)—4 By distilling fuming HNO₃ at a low temperature, and fractionating the distillate in a stream of dry O (Fritzsche, J pr 22, 21) Setlick (C C 1888 461) has determined the yields of NO₂ obtained by the various processes

Properties -At temperatures below -10° a white, crystalline (? prismatic), deliquescent solid, between -10° and 216° a liquid, which is nearly colourless at -9° , yellow at 0° , and orange at 21°, at temperatures above 216°, a gas, the colour of which deepens from orange yellow to nearly black as temperature rises c 180°-200° decomposition to NO + O begins and is complete at c 620° (Richardson, C J 51, 397, cf Reactions, No 1) The colourless liquid is N₂O₄, as this dissociates into NO₂ the colour be comes deeper and deeper red (v Salet, C R 67, 488, also v supra) The gaseous compound at ordinary temperatures is a mixture of NO, and N₂O₄, this gas is reddish brown, has a pungent odour, is irrespirable, and stains the skin yellow NO₂ dissolves in cold water, forming HNO₂Aq and HNO.Aq, it is dissolved, apparently without change, by CHCl₃, C₆H₄Cl, CS₂ (Friedburg, C N 47, 52), and C.H.NO. As solution of NO. in HNO. does not show the absorption-lines of gaseous and liquid NnO2n it is probable that the solution in HNO, contains a compound or compounds of the two substances (Gernez, C R 74, 405) NO probably combines with NO at low temperatures to form N.O. (cf Combinations, No 1)

NO, is an acidic oxide, masmuch as it reacts with H₂O to form HNO₂Aq and HNO₂Aq, because of this reaction it may be looked on as nitrosomitric anhydride, or perhaps better (as there is no nitrosomitric acid) as a mixed anhydride. There are no salts corresponding with NO₂. Numerous nitro compounds are known, obtained by substituting the monovalent radicle NO₂ for

Reactions —1 Heat dissociates N₂O₄ to 2NO₂ (v beginning of this article) At c 180° a 755 mm decomposition to NO+O begins, at c 400° about 83 p c of the NO₂ is decomposed, at c 500° 60 p.c. is decomposed, and at c. 620° the change is complete, on cooling, the NO+O recombine to form NO₂ (Richardson, C J 51, 897) — 2 Electric sparks are said to decompose NO₂ to N and O, according to Richardson (C J 51, 402) a very small quantity of a white solid is produced —3 NO₂ dissolves in water, added to a little ice-cold H₂O a green solution is obtained, which becomes blue on dilution, and then colour-

666 NITROGEN.

less, the solution gives the reactions of HNO. and HNO, On warming NO2Aq, or on adding NO, to hot water, NO is evolved and HNO, Aq (3NO₂ + H₂O + Aq = 2HNO₂Aq + NO)The cold colourless solution of NO2 in water may be raised to the boiling-point without a complete decomposition of the HNO2Aq to HNO3Aq and NO, addition of Pt wire or powdered glass, &c, causes decomposition of NO₂Aq with evolution of NO. NO₂Aq decomposes HIAq and iodides in solution with separation of I, it also deoxidises KMnO4Aq-4 With aqueous solution of an alkah NO2 produces a nitrite and a nitrate 5 Sulphydric acid in solution absorbs NO, evolving NH_3 and depositing $S - 6 NO_2$ passed into conc sulphuric acid forms HNO. and nitrosyl sulphate (lead chamber crystals, 80₂ OH ONO) (v Lunge, D P J 233, 65) -7 NO, dissolves in very conc nitric acid, forming a yellow liquid, which is probably not merely a solution of NO2 in HNO3, masmuch as it does not show the absorption-lines of gaseous or liquid N₂O₄, whereas a solution in CS. does show these lines (v Gernez, C R 74, 465) -8 NO₂ reacts with many carbon compounds replacing H by NO2, with alcoholic wouldes it usually produces nitrates of the alcoholic radicle, eg $C_2H_3I + N_2O_4 = C_2H_3NO_2 + NO + I - 9$ With cold boron chloride, crystals BCl3 NOCl are formed (Geuther, J pr [2] 8, 854)—10 Carbon monoxide is said to be partly oxidised to CO₂, while part of the CO combines with NO₂—11 When NO2 is mixed with hydrogen, and the mixed gases are passed over spongy Pt, H2O and NH3 are formed -12 Ordinary combustibles are extinguished in NO2, but strongly burning phosphorus and carbon continue to burn -13 Many metals decompose NO2, forming oxides and N, Fe, Cu, &c, at a red heat, K and Na at the ordinary temperature—14 Liquid N₂O₄ reacts with mer-cury to form HgNO₃ and NO without any nitrite, the equation $2N_2\ddot{O}_4 + 2Hg = 2HgNO_3 + 2NO$ is almost realised quantitatively (Divers a Shi midzu, C J 47, 630) With silver, liquid N2O4 forms AgNO₃, copper probably forms $Cu_2(NO_3)_2$ (D a S, lc) —15 Liquid N₂O₄ reacts with liquid sulphur discrete to form $(NO_2)_2 S_2O_5$ (De la Provostaye, A Ch [3] 73, 362) -16 With sulphurec anhydride, NO, gas forms
NO, S₂O, O NO₂ (Weber, P 123, 337)
Combinations —1 With nitric oxide, at low

temperatures, to form a blue liquid which is chiefly N₂O₃ (Dulong, A Ch 2, 317, Peligot, A 39, 327, Ramsay, C J 57, 590, Richardson, C J 51, 397) Ramsay a Cundall (C J 47, 672) found that no contraction occurs when dry NO2 and NO are mixed at the ordinary temperature According to Hasenbach (J pr [2] 4, 1), N₂O₃ is formed by passing NO and NO₂ through a hot tube, and then into a well-cooled receiver —2 With chloring, and bromine, to form NO₂Cl, and NO₂Br, respectively (Gay-Lussac, A. Ch. [8] 23, 203, Landolt, A 116, 177, but denied by Williams, C J 49, 226) -8. With antimonic chloride, to form 8SbCl₂N₂O₄, obtained by heating in a sealed tube at 100° (Besson, C R 108, 1012) —4 NO₂ also combines with the chlorides of aluminium, antimony (SbCl2), bismuth, and iron, the compounds are decomposed by water, and also by a gentle heat (B, lc) —5 With phosphorus pentafluoride, to form crystals of NO₂PF₅, very

easily decomposed (Tassel, C R 110, 1264) -6 Witn magnessum hydrogen phosphate, to form 2MgHPO, NO, (Luck, Fr 1874 255) -7 With amylene (and some other hydrocarbons) to form C₃H₁₀(NO₂)₂
Constitution of N₂O₄—From the reactions of

liquid N₂O₄ with Hg and Ag, whereby HgNO₃, or AgNO₁₁ and NO are produced, Divers a Shimidzu conclude that N_2O_4 is best represented as NO NO_3 (C J 47, 630) This formula is in keeping with the reaction AgO NO+NO2Cl = AgCl+NO ONO2 (Exner, C C 1872, 273), this argument, how ever, assumes AgNO₂ to have the structure AgO NO (v Nitrites, p 567), it also assumes the existence of NO₂Cl The formation of nitrosyl sulphate by the reaction of N₂O₄ with H₂SO₄ is also in keeping with the formula $NO NO_3$, $NO NO_3 + H_2SO_4 = NO HSO_4 + HNO_3$ Also, if nitrous acid is assumed to be HO NO, then the formation of this acid and HNO, by the re action of N2O4 with water points to the formula $NO ONO_2 (NO ONO_2 + H_2O = NO OH + HO NO_2)$ The formation of diazo benzene nitrate by the reaction of N₂O₄ with amido benzene is in keeping with the formula NO ONO₂, thus C₆H₅ NH₂+NO ONO₂ = NO₂ O N N C₆H₅+H₂O
The formation of C₂H₃ ONO₂ by the reaction of NO mathematical states of the control NO4 with C2H3I is best expressed by writing NO₄ as NO ONO₂ $(C_2H_5I + NO ONO_2 = C_2H_5 ONO_2 + I + NO)$ The fact that $C_5H_{10}(NO_2)_2$ when reduced by Sn and HClAq yields NH₄Cl and not an NH₂ compound. induced V Meyer (A 171, 5) to assign to N_2O_4 the formula NO O_2 NO, and to write C_5H_{10} (NO₂), as C_bH₁₀(ONO)₂, because had the C been in direct union with N, an NH2 compound would have been formed on reduction N₂O₄ is dissociated by heat to 2NO2, this reaction seems to point to the constitution O2N NO2, or perhaps to NO O2 NO Whichever formula is adopted, the reactions of N₂O₄ make it evident that some substances separate the group NO2, and others the group ONO, and that the way in which the molecule N2O4 splits up depends largely on the conditions of the reaction

NITROGEN PENTOXIDE N.O. (Nitric anhy dride) Mol w uncertain, as compound has not

been gasified

been gashied

Formation —1 By passing Cl over AgNO $(2\text{AgNO}_{\bullet} + \text{Cl}_2 = 2\text{AgCl} + \text{N}_2\text{O}_3 + 0) = 2$ By deby drating cone HNO₃ by $P_2\text{O}_3$ $(2\text{HNO}_3 + P_2\text{O}_5 = 2\text{HPO}_3 + \text{N}_2\text{O}_5) = 3$ By the reaction of NO₂Cl on AgNO₃ at $60^\circ - 70^\circ$ $(\text{AgNO}_3 + \text{NO}_2\text{Cl} = 2\text{AgCl} + \text{N}_2\text{O}_5)$ odet a Vignon, CR 69, 1142, 70, 96, but the existence of NO₂Cl is very doubt ful, V Williams, O J 49, 226)

Preparation —1 Perfectly dry AgNO 10

Preparation -1 Perfectly dry AgNO, 18 placed in a dry U tube, which is connected by a glass tube, without corks or caoutchouc, with another dry U tube having a small reservoir at the bottom, the U tube containing AgNO, is immersed in a water bath, and the other U tube is surrounded by ice and salt, a very slow stream of dry CO2 is passed through the appa ratus, the AgNO, being kept at c 180° (to expel every trace of moisture), a very slow stream of dry Cl is then passed from a gasholder (the Cl being stored over conc H2SO, and driven out by the inlet of H2SO4), the AgNO, being heated to 95°, and the temperature then lowered to 58°-68°. After a time crystals of N₂O₄ appear NITROGEN 567

in the cooled U tube, while a little liquid (N2O4 or N₂O₃) collects in the small reservoir more than 3 to 4 litres Cl should pass in 24 To transfer the N2Os to another vessel, the Cl is replaced by a current of dry CO, the U tube is connected by a glass tube with the vessel, which is immersed in a freezing mixture, the U tube is removed from its freezing mixture, and the N_2O_3 is poured into the vessel (Deville, A Ch [3] 28, 241) -2 Very cone HNO₃ is surrounded by ice and salt, rather more P.O. than the wt of HNO3 is added little by little, so that the temperature does not rise above 0°, the thick mass is brought into a wide retort and distilled at as low a temperature and as slowly as pos sible, the retort being cooled if the liquid froths, pure N.O. condenses in the cooled receiver, but towards the end of the reaction liquid 2N2O3 H2O is formed (Berthelot, Bl [2] 21, 53, a modifica tion of the process given by Weber, J pr [2] 6, 342) About 80 grams N2O5 are obtained from 150 gr HNO_s

Properties and Reactions —Very lustrous, translucent, rhombic prisms, melts c 30°, with partial decomposition to N,O, and O, and boils between 45° and 50° N,O, should be kept in stoppered bottles over H,SO, At c 15° the crystals become yellowish, but are colourless when kept in a freezing mixture (Weber, 1c) S G c 164 H F [N²,O³] = -31,600 (Berthelot, A Ch [5] 6, 145), [N²,O³,Aq] = 29,820 (Th 2, 199), N,O, decomposes slowly when kept, rapidly in sunlight, giving N,O, and O (Berthelot, Bi [2] 21,53) Burning P burns brightly in slightly warmed N,O, C burns in the vapour of N O, but not in the solid or liquid compound, K burns brightly, but most of the metals are without action on N,O,, with S there is formed (NO₁),S,O, (Weber, 1c) N,O, reacts with water to form HNO₂ With cone HNO₃, it produces H,N,O₁ (=2N₂O, H,O, or N,O, 2HNO₃, v Diritic acid, under Nitric acid, p 520) The reactions of N₂O, point to the constitution NO₂ O NO, Pernitric oxide NO₃ or N₂O, According to

PERNITRIO OXIDE NO₃ or N₂O₆ According to Hautefeuille a Chappuis (C R 92, 80, 134, 94, 1111, 1306), a very unstable compound of this composition is obtained by the action of the silent electric discharge on a mixture of N and O at a low temperature. When a certain quantity is formed, the substance begins to decompose to NO₂ and O Berthelot (Bi [2] 35, 227) says that the compound is obtained by the action of the induction discharge on a mixture of O and NO₂. The compound is described as a liquid which does not solidify in a freezing mixture of ice and salt, and is extremely untitable decomposite NO₂ and O.

stable, decomposing to NO, and O
Nitroges, oxyscids of The only oxyscids
of N which have been isolated are nitric (HNO₂)
and dinitric (H₂N₁O₁), nitrous soid (HNO) and
hyponitrous acid (H₂N₂O₂) are known in aqueous
solution Nitric and dinitric soids are described
under the heading Nitrate acid (p 517) The
present article contains descriptions of nitrous
and hyponitrous acids and their salts

Nitrous acid and Nitrites, HNO₂Aq and M¹NO₂ Nitrites are usually, if not always, accompanied by nitrates in nature. Nitrites are present int he atmosphere, Warington (C J 89, 229) has shown that when distilled water is exposed to the air it soon gives the reactions of

nitrites Small quantities of nitrites are present in many river and well waters (v Warington, C J 55, 537, Munro, C J 49, 632) The juices of many plants contain nitrites (Genadius, Am Ch 5, 7) Nitrites are sometimes, but not generally, found in saliva (Wurster, B 22, 1901) Nitrites are formed in the soil by oxidation of various nitrogenous compounds (v Nitrifica TION, p 521) NaNO2 is formed by exposing Pt black to air and NaOHAq (Loew, B 23, 1443) NH₄NO₂ is produced by passing O and air over Pt black at 180°-300° (Ilosva, Bl [3] 2, 734) NH,NO₂ is also produced by burning H in air (Struve, J 1870 199, 209, Schönbein, J 1862 94, Zöller a Grete, B 10, 2145), and also during the slow combustion in air of P or ether (Berthelot, A Ch [5] 12, 440, C R 108, 543, Kolbe, A 119, 176, Ilosva, Bl [3] 2, 734) It was formerly stated that NH, NO, is formed by the direct union of N and H₂O (by evaporating H2O in air), but this has been disproved (Carius, A 174, 31, Weith a Weber, B 7, 1745), Ber thelot, however, asserts that NH, NO, is produced by subjecting H2O and pure N to the action of a very powerful induction coil (Bl [2] 27, 338) NH,NO₂ is also formed by the oxidation of NH, by ozone (Carius, lc, Goppelsröder, J pr [2] 4, 139, 383) Fe nitrite is said to be formed by passing air over reduced Fe at 190°-250° (Ilosva, Bl [3] 2, 734) Alkalı nıtrıtes are formed, along with nitrates, by the reaction of N O₃ on alkalı solutions (v. Nitrogen trioxide, Reactions, No 2, p. 564) Nitrous acid, along with HNO, is produced by the action of cold water on N.O. (v. Nitrogen trioxide, Reactions, No. 1, p. 564) Nitrites are also formed by the reduction of nitrates, eg by heating KNOs, O is evolved and KNO2 remains, or by the action of amalgamated Zn on KNO, Aq, KNO, Aq is pro duced

The normal nitrites have the composition $M^{I}NO_{2}$ and $M^{II}(NO_{2})_{2}$, several basic nitrites are known Most of the normal nitrites are soluble in water and alcohol, AgNO, is one of the least soluble nitrites, from it most of the other nitrites may be obtained Nitrites are decomposed by heat, evolving NO or NO2, and leaving metallic oxide or metal, solutions of nitrites are decom posed by boiling, generally with evolution of NO and formation of nitrates Nitrites in solution are decomposed by dilute H2SO,Aq, giving HNO, Aq, which soon decomposes to HNO, Aq Acidulated solutions of nitrites reduce and NO KMnO₄Aq, K.Cr₂O₇Aq, H₂SAq, &c, they ppt Au from AuCl₃Aq, and Hg from mercurous solu These solutions decompose KIAq with separation of I, and give a brown colour with FeSO, Aq, these reactions serve to distinguish nitrites from nitrates (For details regarding the detection and estimation of nitrites, a manual of analysis must be consulted) Nitrites may be regarded either as MO NO or as M NO,, Divers (C J 47, 226) endeavours to show that the second view is preferable

Nitrous acid HNO2Aq This said is known only in aqueous solution, and it is doubtful whether HNO2Aq has been obtained free from HNO2Aq Fremy (C R 79, 61) says that a solution of N2O4 in a considerable quantity of cold water may be kept for some days without change, and that on boiling NO and N2O4 are

evolved. The solution very probably contains HNO, but whether it is free from HNO, or not is undecided This solution acts as a strong reducer Thomson gives the thermal data [N2,O2,Aq] = -6,820, $[H,N,O^2,Aq] = 30,770$, [2NO,O,Aq] = 36,330, [H,NO,O,Aq] = 52,345 (Th 2, 199)

Netretes MINO2 and MII(NO2)2, also basic salts, $xMOyN_2O_3$, and $xM_2O_3yN_2O_3$ nitrites have been examined chiefly by Fischer (P 74, 115), Lenz (P 118, 282), Hampe (A 125, 295), Stromeyer (A 96, 230), Lang (J pr 86,

299)

Ammonium nitrite NH₄NO₂ A crystalline mass, decomposed by heat to N and H₂O (v NITROGEN, Preparation, No 2, p 557) Obtained by decomposing NH₄ClAq by AgNO₂Aq Berthelot (Bl [2] 21, 55) says this salt is formed, along with N, by the action of dry NH, on NO and O It was formerly stated that NH, NO, 18 produced by evaporating water in air free from NH, but this was disproved by Carius (A 174, 31) and by Weith a Weber (B 7, 1745) According According to Berthelot (Bl [2] 27, 238) NH, NO, 18 produced by the action of a powerful induction coil on a mixture of H₂O and pure N NH₄NO₂ is also formed by oxidising NH₈Aq by ozone (Carius, lc, Goppebröder, Jpr [2] 4, 139, 383), and also, along with ozone and H_2O_2 by burning H ın air (Struve, J 1870 199, 209, Zöller a Grete, B 10, 2145)

Barrum nitrite Ba(NO₂), H₂O (Fischer) Cadmium nitrite Cd(NO2)2 H2O (Hampe, Lang).

Calcium nitrite Ca(NO2)2 H2O (Fischer,

Hampe, Lang)

This salt is not known, but Cobalt nitrite several double salts of Co(NO2), have been isolated.

Cobalt-potassium nitrite

2Co(NO₂)₂ 6KNO₂ xH₂O (x varies from 0 to 1, 3, and 4) Prepared by mixing KNO₂Aq and Co(NO₃)₂Aq, or CoCl₂Aq, adding excess of acetic acid, washing the pp with K acetate solution, and then with 80 pc alcohol, and drying below A bright yellow powder, consisting of small 4 sided prisms, very slightly sol water, insol alcohol or ether At 200° gives NO_2 , Co_2O_2 , and KNO₂ (Fischer, P 67, 245, Saint-Evre, J pr 54, 85, 58, 185, Braun, Fr 6, 42, 7, 313, Stromeyer, A 96, 220, Erdmann, J pr 97, 385, Sadtler, Am S [2] 49, 189) Various other Co-K nitrites are formed under different conditions of concentration and acidification (v especially Sadtler, lc) If Ca salts are present a triple natrite of Co, Ca, and K is ppd (Erdmann, lc) A triple nitrite of Co, Pb, and K is described by Stromeyer (lc) Erdmann (lc)also describes a compound of Co(NO2), KNO2, and NH.

Cobalt-cæsium nitrite Co(NO₂), 3CsNO₂, H₂O (Rosenbladt, B 19, 2531) Cobalt-sodium nitrites

2Co(NO2)3.4NaNO2.H3O and $2Co(NO_2)_3.6NaNO_2.H_2O$ (Sadtler, lc)

Copper mitrites, basic salts (Hampe, van der

Meulen, B 12, 758)

Lead nitrites These salts were examined by Proust, Chevreul (G A 46, 176), and Berzelius (G A 40, 194, 46, 156) Péligot (A 89. 838) revised and classified the work, Bromeis (A 72, 88), von Lorenz (W A B [2nd part] 84

1133), and Meissner (J Z [2] 3, 26), more recently have examined these salts The lead nitrites are all basic salts, many seem best looked on as compounds of basic nitrites with basic nitrates They are obtained by digesting Pb(NO_s)₂Aq with Pb, von Lorenz says that 14 different salts are thus obtained

Magnesium nitrite Mg(NO₂)₂ 3H₂O (Lang);

 $Mg(NO_2)_2 2H_2O$ (Hampe)

Mercuric nitrite Hg(NO₂), 2HgO H₂O (Lang) Nickel nitrite Ni(NO₂), (Lang) The double salts, N1(NO₂)₂ 4KNO₂, N1(NO₂)₂ 2KNO₂ Ba(NO₂)₂, N1(NO₂)₂ 2Ba(NO₂)₂, N1(NO₂)₂ Ca(NO₂)₂ 2KNO₂ have been isolated (Erdmann, J pr 97, 385)

Platino-nitrites v PLATINUM, vol 1V

Potassium nitrite KNO₂ Colourless, micro scopic, prismatic crystals (according to Lang, J pr 86, 295, the crystals are 2KNO, HO, very sol water, insol absolute alcohol KNO Aq with H2SO4 evolves NO, and forms KNO3Aq KNO, is prepared by passing into cold KOHAq the gas obtained by heating starch with HNO, Aq S G 1 35, evaporating till crystallisation begins, pouring off from the crystals of KNO, adding dilute acetic acid and 2 vols alcohol, separating the lower layer which forms and evaporating it (Fischer) Stahlschmidt (P 128, 466) reduces KNO₃Aq by Zn in presence of NH₃Aq Erdmann (J 1866 154) reduces KNO_3 by fusion with Fe, and crystallises from water

Double salts of KNO with the nitrites Ba, Cd, Ca, Co, Cu, Pb, Mg, Hg N1, Pd, Ag, Sr, and Zn are described by Hampe, Lang, and Fischer

Silver nitrite AgNO, Obtained by adding AgNO, Aq to the solution produced by passing into KOHAq the gas formed by heating starch with HNO, Aq S G 135, after neutralising this solution by acetic acid Small white crystals Dissolves in 300 pts water at ordinary tempera tures, easily in boiling water The decomposi-tion of AgNO₂ by heat has been examined by Divers a Shimidzu (C J 47, 630) with H₂S, AgNO, yields Ag₂S, S, NO, NH₃, and NH₂OH (Divers a Haga, C J 51, 48)

Sodium nitrite NaNO₂. A crystalline salt, prepared similarly to KNO₂. Etard (Bl [2] 27, 434) recommends to fuse NaNO, with an equi valent quantity of K2SO4, and to extract with

alcohol.

Strontrum nutrite Sr(NO₂)₂ (Hampe)

Zinc nutrite Zn(NO₂)₂ 8H₂O (Lang, Hampe)

Hyponitrous acid and Hyponitrites,

N₂O₂Aq and M₂N₂O₂. Hyponitrites were first H₂N₂O₂Aq and M₂N₂O₂ Hyponitrites were first obtained by Divers in 1871, by reducing nitrates by Na-amalgam (Pr 19, 425) The salts were examined by Zorn (B 10, 1306, 11, 1630, 2217, 12, 1509, 15, 1007, 1258), van der Plaats (B 10, 1507), Menke, (C J 33, 401), Berthelot a Ogier (C R 96, 30, 84) In 1884 Divers and Haga (C J 45, 78) showed that the silver salt is nAgNO The investigation has been con tanued by Divers and Haga (C J 47, 364, 55, 760), Dunstan and Dymond (C J 51, 646), and Berthelot and Maquenne (C R 108, 1286, 1803)

Zorn prepared ethyl hyponitrite and determined its molecular formula (from VD) to be $(C_2H_3)_2N_2O_2$, hence the formula for the salts is better written M₂N₂O₂ than MNO

Hyponitrites are produced (1) by reducing

NITROGEN 569

nitrates or nitrites in solution by Na amalgam (Divers), (2) by electrolysing nitrite solution, using Hg as negative electrode (Zorn., Divers a Haga), (3) by the reaction of Fe(OH), on alkaline nitrite solution, or on NO in presence of alkalı (Zorn, Dunstan a Dymond), (4) by decomposing oxyamidosulphonates [salts of

NH(SO,H) OH] by alkalı (Divers)

Silver hyponitrite Ag₁N₂O₂ (Nitrosyl silver) Preparation—1 Na amalgam is added to KNO, Aq in the ratio KNO, 4Na, the liquid being kept cold When evolution of gas ceases the solution is neutralised by acetic acid, and AgNO_s is added, the pp is washed in the dark with cold water, dissolved in cold dilute HNO,Aq, and reppd by Na,CO,Aq, the pp is thoroughly washed in the dark and dried in vacuo over ${
m H_2SO_4}$ (Divers, Pr 19, 425, D a Haga, C J 45, 78) -2 Zorn (B 12, 1509) reduces ${
m Ba(NO_2)_2}$ by Na amalgam, and ppts by AgNO, Aq, the pp of Ag₂N₂O₂ thus obtained is pure The Ba(NO₂)₂ is obtained by boiling Ba(NO₃)₂Aq with Pb, prepared by ppg dilute Pb acetate solution by Zn, the boiling is continued till all the Pb is changed to PbO, the PbO in solution is removed by CO2, and the last traces by H2S, the filtrate is evaporated to a thick oil, which cools to a mass of Ba(NO2)2, the salt is obtained pure by crystallising from 80 p c alcohol For preparing large quantities of Ag₂N₂O₂, Zorn (lc) places the Na amalgam, in large pieces, in the middle bulb of a Kipp's apparatus, the Ba(NO₂)₂Aq being in the lower bulb, and the upper he half fills with distilled water By regulating the stopcocks so that a slow stream of gas escapes, the reduction proceeds satisfactorily—3 Pure FeSO₄Aq is mixed with enough milk of lime to ppt the Fe as Fe(OH)2, NaNO2Aq 1s added (1 part NaNO2 to 10 parts FeSO,), and the apparatus is kept cold When the reaction is finished the solution is ppd by AgNO₂Aq (Zorn, B 15, 1258, cf Dunstan a Dymond, C J 51, 646)

Properties and Reactions—Ag₂N₂O₃ 18 a

By standing in yellowish amorphous salt NH₃Aq over H₂SO₄, it is obtained in small crys tals (Zorn) The salt is not hygroscopic, insol water, may be kept in boiling water without decomposition, is decomposed at c 100°, probably giving AgNO, when quickly heated to c 150°, Ag, N,O, explodes, evolving brown vapours Ag,N,O₂ dissolves in HNO₃Aq and H₂SO₄Aq, it is reppd by NH₃Aq or Na,CO₃Aq Unacted on by $\tilde{\text{CO}}_2$ Decomposed by NaOHAq at c 70° Decomposed by H,PO,Aq, H,S, or boiling H C₂H₃O₂Aq, with production of H₂N₃O₂Aq Ag₂N₂O₂ reacts with C₂H₃I to form (C₂H₃)₂N₂O₂ (Zorn, B 11, 1630), the formula of which compound is molecular, as its VD has been deter-

Barrum hyponitrite BaN,O, is described by Zorn (B 15, 1007)

Calcium and Strontium hypomitrites

CaN2O24H2O and SrN2O25H2O are described by

Maquenne (O R 108, 1838)

Hyponitrous acid H₂N₂O₂Aq Known only in solution Moist Ag₂N₂O₂ is suspended in water, such a quantity of dilute HClAq is added that a little Ag₂N₂O₂ remains unchanged, and the liquid is filtered from AgCl (van der Plaats, B 10, 1507). H₂N₂O₂Aq is an acid liquid, fairly stable, may be boiled with HNO₂Aq or

H C.H.O.Aq without decomposition, reduces KMnO,Aq, and separates I from KIAq solution slowly decomposes, and after a few weeks not a trace of $H_2N_2O_2$ remains Inquid thus obtained is neutral, probably N_2O and H₂O are formed It was proved by van der Plaats (lc) that conc H.SO, evolves N.O from

H2N2O2Aq

Constitution of hypometrites —The compound (C2H3)2N2O2 reacts not as an ethereal salt but as a diazo compound, with reducers it evolves N and forms C₂H₅OH, water produces C₂H₅OH, CH₃ CHO, and N The constitution of this compound is C2H5 ONNOC2H5, and hence the constitution of the acid is probably HO N N OH (Zorn, B 11, 1630) This formula is confirmed by the production of hyponitrites, along with sulphites, by the action of KOHAq on NH(SO,K) OH This reaction shows that the O in hyponitrites is in direct union both with N and H (Divers a Haga, C J 55, 760)

Nitrogen, oxybromide of, NOBr (Nitrosyl bromide) Mol w not determined directly, probably = 109 72, from analogy with NOCl very dark brown liquid Obtained by passing NO into Br at -7° to -15° (Landolt, A 11o, 177), also by distilling nitrosyl sulphate (NOH SO.) with KBr (Girard a Pabst, Bl [2] 30, 531) Landolt gives bp as -2° , Girard a Pabst as 19° Easily decomposed to NO and Br by heat With cold water forms HBrAq and HNO, Aq, with KOHAq forms KBrAq and

KNO₂Aq

Nitryl tribromide Landolt (A 116, 117) supposed that a compound NOBr, is obtained (along with NOBr) by passing Br into well-cooled Br That the amount of NO absorbed by Br, at c 15°, is nearly independent of pressure, and corresponds approximately with the quantity required to form NOBr_s, was shown by Pattison Muir $(C \ J \ 28, \ 844)$ The experiments of Frohlich (A 224,270), and of Roozeboom (R T C 4, 381) have shown that the so called nitryl tribromide is probably only a mixture of NOBr and

Nitrogen, exychlorides of The compound NOCl has been isolated, the existence of NO2Cl is very doubtful, according to Hautefeuille a Chappuis (A Ch [6, 2, 282), a compound N2Cl2O is formed by passing N with O and Cl through an induction apparatus The non existence of NOCl., said by Gay Lussac to be produced by the reaction of conc HClAq with HNO, (A Ch [3] 28, 203), has been proved by Tilden ($C\ J$ 27, 683), and this has been confirmed by Gold-

schmidt (A 205, 372)

NITROSYL CHLORIDE NOC! (Chlorontrous gas) Mol w 65 34 VD 33 at c 15° to 700° (Sud-1438, at -12° 14165 (Geuther, A 245, 97 Tilden, C J 27, 630) Boils at c -8° (Tilden) An orange red gas, liquefied by passing through a U tube cooled by ice and salt, the liquid is reddish yellow Dissociation into NO and Cl reddish yellow Dissolution in the arc and call to begins at a 780°, at 985° about 42 p o is dissoluted (S a M, 1c) For absorption-spectrum v Magnanini (Z P C 4, 427) Formed by combination of NO with Cl (Gay-Lussac, A. Ch [3] 28, 203), by the reaction of POl, POl, or AsCl, with NO, or NO, and by the reaction of POCl, with KNO. (Naquet, J 1860 102), by passing

570 NITROGEN.

HCl into N.O. at a low temperature by heating ! conc HClAq and HNO, and by heating NO H 80, with NaCl

NOCI is more readily prepared by warming HNO₂Aq S G 142 with c 4 vols HClAq S G 116, passing the gases over CaCl₂ and then into conc H.SO, until the acid is saturated, then adding perfectly dry NaCl, and heating gently (Tilden, C J 27, 630, of Girard a Pabst, Bl [2] 80, 531)

NOCl reacts with H2O to form HClAq and HNO2Aq, with KOHAq it produces KClAq and KNO2Aq, Hg decomposes it, forming NO and HgCl, it dissolves Au and Pt more slowly (Tilden, lc) With cone H₂SO₄, introsyl sulphate (NO H SO₄) is formed (Tilden) NOCl reacts energetically with SO, to produce NO, SO, Cl (Weber, P 123, 883) Forms double compounds with many metallic chlorides, e.g. AlCla,

SbCl₂ (v Sudborough, C J 59, 655)

NITRYL CHLORIDE NO2CI compound with this composition was supposed to be formed by the reaction of POCl₃ with AgNO₃ or Pb(NO₃)₂, also by passing a very slow stream of Clover AgNO. at c 95° (Odet a Vignon, C R 69, 1142, 70, 96), Hasenbach obtained a liquid which he took to be NO₂Cl by passing Cl and NO₂ through a hot tube and cooling the issuing gases (J pr. [2] 4, 1), Williamson (Pr 7, 15) poured SO, OH Cl on to KNO, and obtained a gas which formed HNO₃Aq and HClAq with cold water, and was supposed by W to be NO₂Cl, Muller (A 122, 1) supposed that NO₂Cl was formed by the reaction of NO₂ with PCl₃, and Schiff thought he had obtained the compound as a product of the reaction of HNO, with PCl₅ Meissner (J Z 10, 27) failed to obtain any NO2Cl by the processes used by Odet a Vignon, Schiff, Muller, and Williamson Geuther (A 245, 96) could not form NO₂Cl by the reaction of PCl₅ with HNO₃, NO₂, or a nitrate Williams (C J 49, 222) showed that NO₂Cl is not produced by the reaction (1) of POCl, with Pb(NO3)2, (2) of POCl₃ with HNO₃, (3) of SO₂OH Cl with KNO₃, (4) of SO₂Cl₂ with KNO₃, he also established a very large probability in favour of the conclusion that the products of the reaction of NO₂ with Cl, at different temperatures, are NOCl, and N₂O₄ holding more or less Cl in solution

Nitrogen, phosphide of, PHOSPHORUS MITRIDE

Nitrogen, phosphochloride of, N.P.Cl. (Phosphorus chloronitride Nitrogen chlorophosphide Phosphorus nitrogen chloride) Mol. VD 1767 (Gladstone a Holmes, w 84718 O J 17, 225, Wichelhaus, B 3, 163) SG 198 (G a H) Melts at c 110° (G a H), at 114° (W); boils at 240° (G a H), at 250°-260° (W) Crystallises in trimetric forms, abc = 4417 1 1 8165 (Groth, B 3, 166), $\frac{\mu-1}{d}$ M = 109 9. (GaH)

Formation -By heating PCl, with NH,Cl,

NH2 or NH2HgCl

Preparation -1 PCl, is saturated with dry NH,, the product is distilled with water, and the crystals which form on the sides of the receiver are washed, dried, and recrystallised from hot ether (Wöhler a Liebig, A 11, 146) —2 A mixture of 1 pt. PCl, and 2 pts. NH₄Cl is heated in

a flask connected with a reversed condenser: the mass gets red, then brown, and the N.P.Cl. sublimes, the compound is dissolved out inether and crystallised, or is blown over in steam (Gladstone, C J 3, 185, modified by Couldridge, C J 53, 898) The yield is not more than 10 p c of the PCl, used —3. An intimate mixture of white pp (NH₂HgCl) and PCl, is gently heated in a flask, the product is treated with water, which dissolves out HgCl, and NH₄Cl, the residue is dried and the N₂P₂Cl₆ is dissolved out (from PCl₃N₂H₄) by ether (Gladstone a Holmes, C. J 17, 225)

Properties - Hard, lustrous, trimetric, crystals, sol alcohol, ether, or CHCla, insoluble in water, but slowly decomposed (G a H, W) Gives off white fumes when heated in air, may be sublimed in H or H₂S Solution in alcohol slowly decomposes, also that in ether if a trace of water is present (even in absence of water, according to Wichelhaus) Is not acted on by I (G), nor by hot H2SO,Aq, HClAq, or HNO,Aq Wöhler a Liebig), decomposed by hot fuming

HNO, (G)

Reactions — 1 Water forms pyrophosphodiamic acid (P₂N₂H₆O₆) and HCl, according to G a H., but W says the products are many and complicated -2 Ammonia or potash decomposes N₂P₃Cl₄ in alcoholic solution, the reaction being similar to that of water (6 a H) —3 Ammona gas passed over melted N₂P₂Cl₂ forms phospham nPN(NH), and HCl (Couldridge, C J 53, 398) —4 Heated with anzline, P₂N₂(NHC₂H₂), as formed to the couldridge of the couldridge of the couldridge of the couldridge. (Hofmann, B 17, 1909, Couldridge, ic), ortho tolundine, and phenythydrazine produce similar reactions (0, lc)—5 Nascent hydrogen forms PH₃ (W, lc)—6 Heated with copper oxide, NO₂ and N are evolved—7 Passed over red hot eron, N is evolved and FeCl, and Fe phosphide remain (W a L)

Nitrogen, selenide of (?NSe) Espenschied (A 113, 101) passed NH_s, diluted with H, over well cooled SeCl4, shook the product with water, and washed the ppd mixture of Se and N selen ide with CS₂ (to extract Se), he thus obtained an orange-yellow powder, which was extremely explosive and very dangerous to handle Analyses pointed to the formula NSe, but E supposed that the substance probably contained H besides N and Se For details of preparation and proper-

ties v Espenschied (l c

Nitrogen, silicide of, v Silicon nitride, in vol 1v

Nitrogen, sulphide of, nNS Mol w un-known SG 21166 at 15° (Michaelis, Z [2] 6,460), 222 at 15° (Berthelot, A Ch [5] 27, 202) Sublimes at 135°, melts at 158°, and decomposes with slight explosions at 160° (M, lc, at 207° according to B, lc) Berthelot (lc) gives [N,S] = -31,900 N sulphide was prepared, but not pure, by Souberran (A Ch [2] 67, 71), Fordos and Gélis obtained it approximately pure (A ${}^{\circ}Ch$ [3] 32, 385), it has been examined further by Michaelis (Z [2] 6, 460), and Demarcay (C R 91, 854, 1066, 92, 726) N sulphide easily explodes when rubbed or struck with a hammer

Preparation.—1 SCl2 or S2Cl2 is dissolved in 8-10 vols CS2, and dry NH2 is passed in , the liquid darkens in colour, and a cochineal red pp is produced, which dissolves after a time and a

brown powder is ppd., passage of NH, is continued until the brown pp dissolves, and the liquid becomes orange-yellow with a few nearly colourless flocks of NH₄Cl floating in it (addition of more NH, decomposes the NS in solution), the liquid is filtered and allowed to evaporate, when orange red NS separates, the NS is collected and washed with CS2, to remove traces Omitting intermediate products, the reaction may be represented approximately as $8NH_a + 3SCl_2 = 2NS + S + 6NH_aCl_a(F a G) -2$ SOCl₂ is surrounded by cold water, and NH₃ is passed into it, after a time the cold water is removed, the solid mass is mixed by a glass rod, and NH, is passed over it as long as absorption continues, the nearly white mass thus obtained is treated with CS2, and the solution on evaporation deposits NS, the insol in CS₂ consists of NH₄Cl, (NH₄)₂SO₂, and polythionates of NH₄ (Michaelis)

Properies—Orange-red, rhombic (or ?tri clinic) crystals, with a faint odour, which becomes more marked at c 120°, the vapour rapidly attacks the mucous membrane of the nose and eyes, detonates at c 160°, explodes violently when rubbed or struck by a hammer, adheres strongly to glass or paper when rubbed thereon, is electric Insol in, but slowly de composed by, water, slightly sol alcohol, ether, turpentine, CS₂ is the best solvent, this solution slowly decomposes

Reactions—1 Water slowly decomposes NS, forming NH,Aq, (NH₂)₂,O₂Aq, and (NH₂)₂,O₂Aq 2 Potash forms NH₃, K₂,O₃Aq, and K₂SO₃Aq—3 Hydrogen chloride produces NH,Cl, chlor ides of S, and probably a compound of NS with SCl₂—4 Chlorine reacts on NS in CHCl, with formation of a compound of S chloride and NS, Demaiçay (C R 91, 854) gives the formula SNCl to the producet, and says that addition of NS to this produces (SN)₃Cl—5 A large excess of sulphur chloride reacting on NS in CHCl, produces a compound of S, N, and Cl, to which Demarçay (C R 91, 1066) assigns the formula S₁N₂Cl—6 Nitric acid forms S,N₃NO₃, and sulphuric acid produces HOl and S,N₃HSO₄ (D, lc, also C R 92, 726)

Combinations — With sulphur dichloride to form several compounds, especially 2NS SCl₂, 4NS SCl₂, and 6NS SCl₂ (Michaelis)

Nitrogen, sulphochloride of NS₂Cl(=N₂S₃SCl₂) According to Soubeiran (A Ch 67, 87, 101), this substance is formed by heating, in a sealed tube at 100°, the compound 2NH₂SCl₂, which is obtained by passing a slow stream of NH₃ into SCl₂ NS₂Cl is a citronyellow solid, decomposed by heat to N, S, and S₂Cl₂, decomposed by water to NH₄Cl and H₂S₂O₃ NS₂Cl is also said to be formed by passing CO₂ into a hot solution of NS in S₂Cl₂ (S., Le). M M P M

NITROGEN GROUP OF ELEMENTS Natro. gen, phosphorus, vanadium, arsenic, niobium, antimony, didymium, erbium, tantalum, bismuth Of these ten elements, N. As, Sb, and Bi are found uncombined, the others occur only in combination N is found in vast quantities in the air, compounds of N and also of P occur in large quantities in rocks and in animal and vegetable matter Compounds of As, Sb, and Bi are widely distributed in minerals, but no very large quantities are found Compounds of V are found widely spread about, but they occur only in comparatively small quantities The com in comparatively small quantities The compounds of Nb, Di, Er, and Ta have been found in but a few minerals, these four bodies are classed among the rare elements. Sb has been known as a metal from about the end of the fifteenth century, and B1 from the sixteenth century, P was prepared in 1669, As in 1694, and N in 1772, V was obtained by Roscoe in 1867, investigations on this element having been carried on from the beginning of this century, Di was isolated in 1842, Nb and Ta were obtained nearly pure in 1864, after a long series of investigations conducted by different chemists from 1801 onwards, researches on Er have been carried on since 1788 to the present day, but the element has not yet been isolated Within recent years great doubt has been cast on the elementary character of D1, and although the in vestigation of Er is yet far from complete it is very probable that the substance known by this name is not a simple body Of the names given to the ten elements, As is derived from the name by which the chief ore of this metal was known in ancient times, N, P, and Di express characteristic properties of the elements, Er is derived from the locality where the minerals were found from which the compounds of this element have been prepared, V, Nb, and Ta are taken from mythological personages, and the origins of the names Bi and Sb are not known with certainty

N is obtained from air by removing the O by hot Cu, or other deoxidiser, P is prepared by heating Ca phosphate with SiO, to combine with the Ca, and C to remove the O, As, Sb, and Bı are prepared by removing O from the oxides by C, V and Nb by reducing the chlorides at a high temperature by H, and Di by reducing the chloride by Na or K, to obtain Ta, the compound Na₂TaF, is reduced by Na, Er has not yet been isolated N is a gas at ordinary temperatures, but has been liquefied at a very low temperature under great pressure, P is a soft solid with a low melting point and not high SG, the other ele ments are hard, lustrous, and metal like, none has a very high S G, Ta = 11 (?) is the heaviest, and all melt at or below a full red heat (M P of V. Nb. and Ta, not determined, Er not isolated) The following table presents some of the chief properties of the ten elements -

Atomic weights 1401 512 94 144 182

One or more compound of each element, except D₁, has been gasified, specifie heat of D₁ only has been determined directly Mol w of N=At w ×2; mol. w of none of the others known

Melting points | - | 600°-700°

0/2	111110	GEN GIWOI	OF EDEME	1110	
	Nitrogen	Vanadium	Niobium	Didymium	TANTALUK
Specific gravities (approx) Specific heats Atomic weight Spec grav (approx) Occurrence and preparation	(liquid) 885 — 158 In large quantity in air Many compounds, especially nitrates and NH, compounds, are widely distributed in large quantities Prepared by removing Offrom air	55 — 91	7 — 13 4 Niobates occur in a few rare minerals Prepared by repeatedly heat ing NbCl, in H	6 5 04563 22 1 Silicate of Di 18 found in seve	11 (?) Tantalates occur with nio- bates in a few rare minerals Prepared by heating K ₂ TaF ₂ with
Physical properties	Colourless,	ın H	Steel grey, lus trous solid	White solid, with slightly yellow tinge, hard, ductile	
Chemical properties	Combines slowly with O underinfluence of electric dis charge, also to a small extent with H At high temp combines with B, Cr, Mg, Si, and V, and perhaps also with Al, Fe, and Zn Com- pounds exhibit most diverse chem proper- ties, oxides are generally acidic, one hydride is strongly alka- line, another is acidic Never replaces H of acids to form salts Forms the oxychlor ide NOCI An allotropic form perhaps exists, proof is not satisfactory Atom is tri- valent in NH,	V ₂ O ₃ , and finally to V ₂ O ₃ , and finally to V ₂ O ₄ . Burns in Cl to VCl ₄ Combines with N to form VN Dissolved by conc H ₂ SO ₄ and HNO ₃ , forms vanadates with molten alkalis Some oxides are basic, e g V ₂ O ₃ , others are basic and acidci, e g V ₂ O ₄ which forms salts with acids and also with alkalis Reacts both as a metal and a non metal Forms oxychlorides VOCl ₂ , VOCl ₂ , and VOCl Does not form a hydride Atom is tetra-	Nb ₂ O ₅ Combines with Cl to NbCl ₂ Sol in cone H ₂ SO ₄ , not in HNO ₃ or HClAq Nb ₂ O ₅ forms niobates with basic oxides, also dissolves in H ₂ SO ₄ , but no definite salts isolated No hydride known with certainty, but there are in dications of existence of hydride Forms anitride Oxychloride is NbOCl ₃ Compounds formed by replacing H of acids by Nb not yet isolated, but probably exist NbF ₅ and NbOF ₅ form many double salts. Atom	D1 ₂ O ₅ D1 ₂ O ₆ exists and acts as a peroxide D1 ₂ O ₅ is basic, easily sol di- lute acids De composes cold water slowly, and hot water rapidly D1 is almost cer- tainly a mix- ture or com pound of two or more else- ments D10Cl is isolated No hydride No compounds gasified.	bines with Cl to form TaCl, Ta ₂ O, forms tantalates with alkalis, seems to have no basic properties Sol only in HFAq, and H ₂ SO ₄ + HFAq Forms a nitride No hydrideknown No oxychlor- ides isolated Atom penta valent in TaCl,

Martin control systems	PHOSPHORUS	Arsenio	Antimony	Erbium	Вимитн
Atomic weights Molecular	30 96	74 9	120	166	208
. .	61 92 and 123 84	149 6 and 299 6	(?) 120 (?) 240		(?) 208 or (?) 416
	Compounds of all these elements, except Er, have been gasified, and S H each, except Er, has been determined directly				
Melting-points (approx) Specific	45°	500° (under pressure)	425°	_	270~
gravities	19	57	67	_	99
(approx) Specific heats Atomic weight	202	083	053	_	0308
Spec grav	16 3	13 2	18		20 5
Occurrence and preparation	Many phos phates occur in large quanti ties and widely distributed in rocks and waters, also in bones and plants Compounds of P with C, N, and O, are found in nerve and brain matter Prepared by heating Ca ₂ (PO ₄) with SiO ₂ and C	Is found native in small quantity, com pounds with S and other elements are widely distributed, but are not found in very large quantities Piepared by reducing As ₂ O ₃ by C	in small quantity, Sb,S ₃ occurs in comparatively small quantities, fairly widely distributed, other compounds also occur sparingly Pre	As silicate in a few rare mine- rals Er has not yet been isolated	Bi found native, chief compounds are Bi ₂ S ₃ and Bi ₂ O ₃ , not found in anylarge quantities, but fairly widely distributed Prepared by reducing Bi ₂ O ₃ by C
Physical properties	Soft, wax like, crystalline so lid, also a red amorphous solid Non con ductor of elec tricity	brittle, ci ystal	White, lustrous, brittle, very crystalline, solid Fair conductor of electricity	Not isolated	White, with slightly reddish tinge, brittle, crystalline, not good conductor of electricity
Chemical properties	1	As,O ₃ , As ₂ O ₅ also known Combines directly with Cl, Br, and I, to form AsX ₃ Oxidised by HNO ₅ to H,AsO ₄ Oxides are acide, and As ₂ O ₅ is also feebly basic Does not form salts by replacing Hof acids Hydride AsH ₄ is scarcely if at all alkaline Exists in two allotropic forms Atom trivalent in	Sb ₂ O ₃ , Sb ₂ O ₅ also known Combines directly with Cl, Br, and I, to form SbX ₃ and SbX ₅ Oxidised by HNO ₃ to Sb ₂ O ₄ and Sb ₂ O ₅ æH ₂ O Oxides are acidic and basic Forms a few salts by replacing H of acids Decomposes steam, evolving H Hydride SbH ₁ is not alkaline Atom trivalent in gaseous molecules	not known, as the metal has not yet been isolated Very probably Er is a mixture or compound of two or more elements Er ₂ O ₃ is basic, no acidic oxide known No hydride known No compound yet gasified	bines directly with Cl, Br, and I, to form BiX, Oxidised by HNO, to Bi3NO, Oxides are basic, Bi ₂ O, acts as a basic

General formulæ and characters of chief compounds MH₂, M=N, P, As. Sb M₂O₂, M=any element of the group except Nb and Ta M₂O₄, M=N, P, V, Nb, Sb, Ta, Bi M₂O₅, M=any of the elements except Er M₂S₄, M=D₂V, A₃S₄S₅ N₂S₄S₅ N₃S₄S₅ N₄S₅ N₅S₅ N any of the elements except Er M₂S₃, M = P, V, As, Sb, Di, B₁ M₂S₃, M = P, V, As, Sb, some other sulphides known, eg NS, VS, TaS₂, no sulphide of Nb or Er isolated MCl₂, M = any of the elements except Er and Ta MCl₂, M = P, Nb, Sb, Ta, some other haloid compounds exist, eg P_2I_4 , VCI_4 , no haloid compounds of Er isolated with certainty HMO_3 , H_2MO_4 , H_3MO_4 , $H_4M_2O_7$, most of these acids exist for M = N, P, V, As, Sb, acids containing Nb and Ta also known, no acids of Di, Er, or Bi isolated M₂8SO₄, &c, M=Di, Er, Bi VO(SO₄), (VO₂)₂(SO₄), &c As₂O₅ xSO₃, Sb₂O₃ xSO₃, &c The hydrides NH₃, PH₃, AsH₃, and SbH₄. VO(SO4),

show a gradation of properties, from the strongly alkaline NH, to the neutral AsH, and SbH, NH, combines readily with acids, PH, only with such strong acids as HI or HCl, AsH, and SbH, do not combine with acids AsH, and SbH, are easily decomposed by heat, while NH, The hyand PH, are stable in this respect drides are all oxidised by mixing with O and heating, NH, being the most difficult to change in this way A hydride of Nb (? NbH) probably exists N forms also the hydrides NaH and N2H4, the former is a fairly strong acid, the

latter is basic Besides PH, two hydrides of P, viz P₂H, and P₄H, exist Regarded broadly, the oxides may be divided into three classes (1) acidic oxides, those of N and P, (2) basic, those of Di, Er, and Bi, (3) acidic and basic, those of V, As, and Sb—acidic and ? basic, oxides of Nb and Ta The distinctly acidic oxides of N are N2O2, NO2, and N2O5, with water N2O2 forms HNO2Aq, and N2O3 forms HNO3Aq, but NO₂ produces both HNO₂ and HNO₃, N₂O may be called the anhydride of H₂N₂O₂, masmuch as it is formed by heating H₂N₂O₂Aq, but the acid has not been obtained from N₂O NO can hardly be classed as acidic or basic, there are compounds in which NO may be regarded as playing the part of the more positive radicle, eg NOCl and NOH SO, and there are others in which NO seems to form the negative radicle, eg (NO)₂H₂, and perhaps NO OH P₂O₃ and P₂O₅ react with water to form H₂PO₃Aq and H₂PO₄Aq respectively, P₂O₄ forms both of these acids The oxides M₂O₃, where M = D₁, Er, or B₁, react with acids to form acids M₂O₃. B1, react with acids to form salts M_2 3X (X = SO_4 , 2NO₃, &c), B1₂O₃ forms salts B1₂ 3X and evolves O, this oxide probably forms bismuthates— Bi₂O₅ xM₂O—when fused with large excess of alkalis, but these bimuthates cannot be isolated V2O2 probably forms salts with acids, the compound $\nabla_2O_s(SO_s)_4$ 2H₂O has been isolated ∇_2O_s with strong acids forms salts $x\nabla_2O_s$ yA (A=acidic oxide, SO_s , &c), and with alkalis it produces salts of the type $xV_2O_4yM_2O_5$ reacts with alkalis to produce vanadates $xV_2O_3yM_2O_5$. it also combines with several anhydrides to form salts xV_2O_5 yA (A = acidic oxide, P_2O_5 , SO₃, &c), the acids HVO₅ and H₄V₂O₇ have been isolated As O, does not form an acid with water, but with KOHAq it produces KAsO₂, As₂O₅ with water | follows -

forms H,AsO, As₂O₃ combines with a few anhydrides of strong acids to form such compounds as α As,O, γ SO. Neither Sb₂O, nor Sb₂O, forms an acid with water, a few unstable salts Sb₂O, M₂O have been isolated, three weakly acidic hydrates of Sb₂O₅ are known, from each of which salts are derived With acidic oxides Sb₂O₃ combines to form xSb₂O₃ yA (A = acidic oxide, SO₃, &c), some of these compounds are fairly well-defined salts, eg Sb₂O₃ 3SO₃ The oxides Nb₂O₅ and Ta₂O₅ form salts when fused with alkalis, xM_2O_5 yM_2O_7 these oxides dissolve in some strong acids, probably with formation of salts, although none has vet been isolated

The oxyacids of the nitrogen elements are numerous, oxyacids of all except Di, Er, and Bı are known The table on p 575 presents the composition of the most marked of the acids, and the relations between them, their corresponding oxides, and their salts, the symbol Aq added to the formula of an acid means that that acid is known only in aqueous solution, M here stands for a monovalent metal, RO = basic oxide gene

rally, including M2O, MO, M2O2

The acids of N and P possess the charac teristics of acids much more fully than any of the other oxyacids of the N elements HNO₃, HPO₃, H₃PO₄, H₄P₂O₇, H₃PO₄, H₃AsO₄, these acids are produced by the reaction of their corresponding oxides with water—the other acids of the N elements are not obtained directly from their oxides, although in many cases the oxides are formed by heating the acids HNO, Aq is a very strong acid, about equal to HClAq, putting the strength or affinity of HNO₂Aq as 100, that of H₃PO₄Aq is approximately about 6, and that of HASOA about 4 One can scarcely give the name acid to the hydrated oxides of Nb and Ta, and it is very doubtful whether Sb O₃ 3H₂O $(=H_aSbO_a)$ can be called an acid It should be remembered that the oxides of Nb and Ta have not been very fully examined

The chief haloid compounds of the nitro gen elements are MX, and MX,, no haloid com-pound of Er has been isolated with certainty, TaX, is not known, and pentahaloid compounds of N, V, As, Di, and Bi have not yet been pre-pared V forms VCl₄, which has been gasified unchanged Most of the haloid compounds are formed by the direct union of their elements, they are decomposed by water, forming HXAq, and oxyacids or hydrated oxides in the cases of N, P, V, As, Nb, and Ta, and oxyhaloid compounds in the cases of Di (? Er) and Bi, SbCl_s gives SbOCl if little water is used, but Sb₂O₂Aq if much warm water is employed

The sulphides, M2S3, of P, V, As, and Sb react with alkali sulphides to form alkali thiosalts, D12S2 and B12S3 show no acidic properties, Er and Nb sulphides have not been isolated, and the sulphides of Ta have been studied but slightly, NS is an explosive compound, which forms NH, salts of thionic acids when treated

with water or potash

The nitrogen elements form Group V of the elements in the classification based on the periodic law This group is composed as

10 V = 51 Nb = 94Ta = 182Even series N=14 $D_1 = 144$ 11 $B_1 = 208$ Odd series P=81 $\Delta s = 75$ Sb = 120Er = 166

Acid	Salts	Corresponding oxide	Remarks
Netwogen H ₂ N ₂ O ₂ Aq	M ₂ N ₂ O ₃	N ₂ O	Acid not formed from N ₂ O, but N ₂ O obtained by heating H ₂ N ₂ O ₂ Aq, and by action of H ₂ SO ₄ on M ₂ N ₂ O ₂ Aq
H NO ₂ Aq	MNO ₂	N ₂ O ₂	Acid obtained by dissolving N ₂ O ₂ in fair quantity of cold water, solution slowly decomposes to HNO ₂ Aq and NO Doubtful whether HNO ₂ Aq has been obtained quite free from HNO ₂
HNO,	MNO,, also M,NO,, and many basic nitrates xN20, yRO, also probably a few acid salts M'NO, xN2O,	N ₂ O ₄	N.O. reacts with water to form HNO,Aq, N,O. obtained by removing H ₂ O from HNO, by P ₂ O ₅
H ₂ N ₄ O ₁₁	None	N ₂ O ₅	Acid formed by adding very conc HNO ₃ to melted N ₂ O ₃ , and cooling
Phosphorus H H ₂ PO ₃	м н,РО,	None	Acid obtained by action of equivalent quantity of H,SO,Aq on Ba(H,PO,), which is produced by P reacting with BaOAq H,PO, decomposes by heat to H,PO, and PH,
$\mathrm{H_2PO_8}$	M HPO ₃ and M ₂ PO ₈	None	H.PO, obtained by H.S on PbPO, in water and evaporation in vacuo H.PO, Aq fairly stable, boiled with H SO, Aq forms H.PO, Aq and H.PO, Aq
$[\mathbf{H_2}\mathbf{H_2}\mathbf{P_2}\mathbf{O_3}]$	M₂ H₂P₂O₅	P ₂ O ₄ (?)	Acid unknown Na salt got by heating NaH ₂ PO ₃ 5H.O to 160°, Pb salt got by heating PbH ₂ (HPO ₃) ₂ to 140° in vacuo
\mathbf{H}_{z} HPO_{z}	M HPO, and MH2PO.	P,O.	Acid obtained by slow action of cold water on P ₂ O ₄ , decom- posed by heat to H ₂ PO ₄ and PH ₃
HPO, H,PO, H,P2O,	M PO ₄ , M,PO ₄ , M HPO ₄ , MH PO ₄ , M ₄ P ₂ O , M ₂ H ₂ P ₂ O ₇	P,O,	Acids obtained by action of water on P ₂ O ₅ . A little cold water gives HPO ₂ , cold water and P ₅ O ₅ in ratio P ₂ O ₅ 2H ₂ O give H,P ₂ O ₇ , much water gives H,PO ₄ , H ₂ PO ₄ heated gives H ₄ P ₂ O ₇ , and this at higher temperature gives HPO ₃ P ₂ O ₅ is not obtained by heating the acids
Vanadrum HVO ₂ , H ₄ V ₂ O,	MVO ₃ , M ₄ V ₂ O , also salts of types M ₃ VO ₄ , M ₂ V ₄ O ₉ , M ₂ V ₄ O ₁₁ , &c	V ₂ O ₅	Acids not obtained directly from the oxide, but V ₂ O ₅ obtained by heating the acids
Arsenic	MAsO ₂ , M ₃ AsO ₃	As ₂ O ₂	As,Os in water does not form an acid, but reacts with alkalis &c to form salts
$\mathbf{H}\mathbf{A}_{\mathbf{S}}\mathbf{O}_{1}, \ \mathbf{H}_{1}\mathbf{A}_{\mathbf{S}}\mathbf{O}_{4}, \ \mathbf{H}_{4}\mathbf{A}_{\mathbf{S}_{2}}\mathbf{O}_{7}$	MASO ₃ , MH ₂ ASO ₄ , M,HASO ₄ , M ₂ ASO ₄ , M ₄ AS ₂ O ₇	As ₂ O,	H,AsO, obtained by action of H ₂ O on As ₂ O ₅ , H ₄ AsO, gives H ₄ As ₂ O ₇ , and at higher temperature HAsO, is formed on heating HAsO, As ₂ O ₅ and H ₂ O are produced

Acid	Salts	Corresponding oxide	Remarks
Niobium xNb ₂ O ₅ yH ₂ O (? acids)	xNb ₂ O ₃ yRO, some be long to types MNbO ₃ and M ₄ Nb ₂ O ₇ , others are more complex	Nb ₂ O ₃	Hydrates of Nb ₂ O ₃ are known, but salts are not obtained by reaction of these with alkalis, but by fusing Nb ₂ O ₃ with alkalis and alkaline car- bonates
Antimony H _s SbO _s (? acid)	МЅЬО₃	Sb₂O₃	H ₃ SbO ₃ is not obtained directly from Sb ₂ O ₃ , but Sb ₂ O ₃ is formed by heating H ₃ SbO ₃ H ₃ SbO ₃ scarcely exhibits acidic properties MSbO ₂ are few, produced by dissolving Sb ₂ O ₃ in alkalis
	M ₂ Sb ₂ O ₃ (? MSbO ₃ MSbO ₂)	? Sb ₂ O ₄	Said to be formed by fusing Sb,O, with alkalis and alka line carbonates
HSbO ₂ , H ₃ SbO ₄ , H ₄ Sb ₂ O ₇	MSbO ₃ , M ₄ Sb ₂ O ₇ , M ₂ H ₂ Sb ₂ O ₇	So ₂ O ₃	Acids are not obtained directly from Sb ₂ O ₃ , but oxide is formed by heating the acids H ₃ SbO ₄ , gives HSbO ₃ at 175°, H ₁ Sb ₂ O is obtained from its salts, it is easily decomposed to HSbO ₃ HSbO ₃ dissolves in KOHAq, but does not form salts thus, MSbO ₇ , obtained by fusing Sb ₂ O ₅ or HSbO ₃ with alkalis or alkaline carbonates M ₄ Sb O ₇ are formed by action of RO on MSbO ₃
Ta ₂ O ₃ 2H ₂ O (? acid)	MTaO ₃ , also complex salts of general form x Ta ₂ O ₃ y RO	Ta O,	Acid not formed directly from oxide, but oxide obtained by heating the acid Salts formed by fusing Ta ₂ O, or H ₄ Ta O, with basic oxides

The division into two families is not marked, the properties of the members of the group vary gradually from N, which is a typical non metal, to Bi, which is distinctly metallic. The properties of these elements and their compounds show that on the whole V, Nb, and Ta form a family, As, Sb, and Bi another family, and N and P a third family. Di and Er have not been much examined, and it is very probable that neither is an elementary substance. For detailed descriptions of the elements and their chief compounds, v Nitrogen, Phosphorus, &c.

ммрм

NITROGLYCERIN v GLYCERIN NITRO-HARMALINE v HARMALINE

NITRO-HEMIPIC ACID v HEMIPIC ACID
NITRO-HEPTANE (?) C,H₁₅NO₂ (193°–
197°) S G ¹² 937 Occurs among the products of the action of HNO₃ (S G 1 38) on light
petroleum oils (95°–100°) (Beilstein a Kurbatoff,
B 18, 2029) Oil, sol warm KOHAq

NITRO-HEPTYL-BENZENE $C, H_1, C_0H_1NO_2$ (178° at 10 mm) Formed by nitration (Auger, Bl. [2] 47, 50) Heavy straw-coloured oil

DI-NITRO-HEPTYLENE C.H.,2(NO.), [182°]
From heptinene and HNO. (S G 13) (Morris, C. J. 41, 175). Tables (from alcohol) Sol alcohol, ether, and benzene, volatile with steam

NITRO HEXADECYL-BENZENE

 $C_cH_4(C_{16}H_{33})NO_2$ Notro cetyl benzene [c 36°] Formed by nutration of cetyl benzene (Krafft, B 19, 2984)

NITRO-p-HEXADECYL TOLUENE

 $C_8H_2(NO)Me$ $C_{16}H_{33}$ [40°] Obtained by nitra tion of hexadecyl toluene (Krafft a Göttig, B 21, 3182)

DI NITEO HEXANE C₅H₁₁ CH(NO₂)₂ Ob tained from hexyl methyl ketone and HNO₄ (Chancel, C R 94, 399) Heavy oil Yields n hexoic acid on reduction —KC₅H₁₁N₂O₄ yellow plates (from hot water) —AgA'

Tetra nutro hexane C₆H₁₀(NO₂), Crystals, obtained by passing NO₂ into an ethereal solution of diallyl at 0° (Henry, B 2, 279)

NITRO-HEXOIC ACID C₆H₁₁NO₄ [112°]

NITRO-HEXOIC ACID C₆H₁₁NO₄ [112°] Formed by reducing di intro hexoic acid in alcoholic solution by sodium amalgam (Kullhem, A 167, 45, Kachler, A 191, 159) Four sided prisms, v sol water and alcohol With tin and HClAq it yields methyl isopropyl ketone, hy droxylamine, and CO₂. On adding H₂SO₄ to a solution of the K salt mixed with KNO₂, there is produced a blue colour, which can be taken up by ether NaA'3aq —BaA', 3aq —BaC₆H₈NO₄.

Di-nitro-hexoic acid C₆H₁₀N₂O₆ [215°]. Formed by boiling camphor with HNO₃ (Kullhem, A 163, 231, Kachler, A 191, 144) Plates (from water) —NH,A' —NaA'4aq —CaA', 3aq slender needles —BaA', 5aq —BaA', 3aq —AgA' Formerly supposed to be C₇H₁₂N₂O₆, v Di nitro heptoic acid, under Camphob, vol 1 p 672

NITROHEXYLENE C₆H₁₁NO₂ (?) 215°) A product of the action of HNO, (S G 134) on the fraction 95°-100° of the petroleum of Baku (Beilstein a Kurbatoff, B 13, 1820)

m NITRO HIPPURIC ACID C,H,N,O, 16 C₆H₄(NO₂) CO NH CH₂ CO₂H [162°] S 36 at 23° Formed by the action of HNO and H CO Formed by the action of HNO₃ and H SO₄ on hippuric acid, and occurs in dogs' urine after administration of m nitro benzoic acid (Berta gnini, A 78, 100, Schwanert, A 112, 69, Con rad, J pr [2] 15, 254) Needles Split up by HClAq into glycocoll and m nitro benzoic acid CaA'₂3aq — BaA'₂—CuA'₂5aq — ZnA'₂6aq — PbA'₂5aq — AgA'

p Nitro hippuric acid C.H.N.O. Occurs in urine after a dose of p nitro toluene (Jaff ℓ , B 7, 1673) Orange prisms (from alco hol) $-\mathrm{BaA'_2}$ 4aq $-\mathrm{AgA'}$ long needles $-\mathrm{Ure}\,a$ salt $\mathrm{HA'CON_2H_4}$ [180°] Occurs in dogs' urine after a dose of p nitio benzoic aldehyde (Sieber a Smirnoff, M 8, 90) Pearly plates

NITRO-HYDANTOIN C3H3N3O, 2 e

NH < CO CH(NO) >[170°] Formed from hydantoin and HNOs (Franchimont a Klobbie, \vec{R} T C 7, 12)

DI p NITRO HYDROBENZOÏN

Acetyl derivative C₆H₄(NO) CH(OAc) CH(OAc) C₆H₄NO₆ From the dibromide of dip nitio di phenyl ethylene and alcoholic KOAc (Elbs a Bauer, J pr [2] 34, 346) Small yellow crystals, m sol alcohol, ether, and glacial HOAc

NITROHYDROCHLORIC ACID v CHLOR-HYDRIC ACID, Reactions, No 17, vol 11 p 8

NITRO-HYDROCINNAMIC ACID v NITRO B PHENYL PROPIONIC ACID

DI NITRO-HYDRO-p-COUMARIC ACID v DI NITRO p OVY β PHENYL PROPIONIC ACID

NITRO HYDRO 4-CUMOQUINONE C.H., NO. ie C₆Me₃(NO)(OH)₂ [106⁻] Formed from nitro ψ cumoquinone and SO₂ (Nef, A 237, 18) Yellow needles (from ether)

NITRO-HYDRO-(B)-NAPHTHOQUINONE C₁₀H₇NO₄ v e C₁₀H₅(NO)(OH) [159 5°] Formed from nitro (3) naphthoquinone and SO (Ziert ling, B 23, 177, cf Groves, C J 45, 299) Red

needles, sol boiling water

NITRO HYDROQUINONE Mono methyl ether C_sH₃(NO₂)(OMe)(OH) [83°] Formed sther C₆In₄(10c)(Constant) and ther (Weselsky a Benedikt, M 2, 369) Orange needles

Di methyl ether C₆H₃(NO₂(OMe), [71°]

Formed from $C_8H_4(OMe)_2$ and cold dilute (1 10) HNO₃ (Habermann, B 11, 1034, Muhlhauser, A 207, 253) Felted needles

Mono-ethyl ether C₆H₄(NO₂)(OEt)(OH)

Output

Property of the content of the

Dr-ethyl ether CoH, (NO2) (OEt)2 Formed by nitration (Nietzki, A 215, 148) Mono-benzyl derivative

C₆H₃(NO₂)(OC₇H₇)(OH) [158°] Formed by boiling the benzyl derivative of nitro arbutin with dilute H2SO, (Schiff a Pellizzari, A 221, 871, G 14, 501) Yellow needles (from water).

 $\begin{array}{c} \textit{Di-benzyl derivative} \\ \textit{C}_{6}H_{3}(NO_{2})(OC_{7}H_{7})_{2} \quad [83^{o}] \quad \text{Obtained by nitration} \\ \textit{of } C_{\underline{6}}H_{4}(OC,H_{7})_{2} \quad \text{Yellow needles (from alcohol)} \end{array}$

Di propiony l derivative C_eH₃(NO₂)(O COEt)₂ [86°] Obtained by nitration (Hesse, A 200, 247)

Di nitro hydroquinone C6H1N2O $C_0H_2(NO_2)_2(OH)$ [5 2 4 1] [136] Obtained by saponification of its di acetyl derivative (Nietzki, B 11, 469, A 215, 145) and also by boiling dinitro arbutin with dilute H2SO4 (Strecker, A 118, 293) Flat golden needles (from water) Its alkaline solutions are violet —BaA"

black needles with bronze lustre Di acetyl derivative [96°] Obtained by nitrating the di acetyl derivative of hydro quinone Yellow needles

Mono methyl ether [102°] Needles
Di methyl ether The two crystalline isomerides C_bH (NO₂)₂(OMe)₂[3 2 1 4] [177°] and C_bH (NO₂) (OMe) [5 2 1 4] [202°] are formed by nitrating CoH4(OMe)2 (Nietzki a Rechberg, B 23, 1216)

Mono ethyl ether [71°] Yellow needles
Di ethyl ether The two crystalline
isomerides C.H (NO) (OEt) [3 2 1 4] [130°] and $C_6H (NO_2)_2(OLt)_2[5\ 2\ 1\ 4] [176°]$ are formed by nitration of the dicthyl derivative of hydroquinone (Nietzki, A 215, 150, N a B)

Methylethylether $C_6H (NO_2)_2(OMe)(OEt)$ $[144^{\circ}]$ Formed from $C_6H_2(NO_2)_2(OMe)(OEt)$ (Fiala, M 6, 914)

Bensyl ether C, H (NO,) (OC, H,)(OH) [137°] Formed by nitration (S a P) Golden needles —KA' aq explosive scarlet needles Loses NH₃ in air, forming C13H10N2O62NH3 NH,A', which is stable

Tri nitro hydroquinone Di methyl ether C_bH(NO₂)₃(OMe) [101°] Formed by adding a solution of C_bH₄(OMe)₂ in HOAc to a cold mixture of H.SO, and fuming HNO, (H) needles (from alcohol)

Dt ethyl ether C,H(NO),(OEt), [130]
Formed from ether C,H (NO),(OEt), by further nitiation (Nietzki) Yellow needles Anilne forms red crystals of C_sH(NO) (NHPh)(OEt)₂ [133°] whence alcoholic potash yields yellow crystals of C₆H(NO₂)₂(OH)(OEt)₂ [152°]

Dr 1sobutyl Tetra nitro hydroquinone ether $C_6(NO)_*(OC_4H_0)_2$ Formed by nitrating $C_8H_4(OC_4H_3)_2$ (Schubert, M 3, 686) Needles (from alcohol), v sol hot HOAc

DI-NITRO HYDROTOLUQUINONE

C₆HMe(NO₂),(OH)₂ [149°-153°] Obtained by saponifying its mono acetyl derivative, which is got by nitrating the di acetyl derivative of hydro toluquinone (Kehrmann a Brasch, J pr [2] 39, Yellowish red crystals (containing aq)

Acetyl derivative C₆HMe(NO₂)₂(OAc)(OH) [146°] Yellow orystals

Dr acetyl derivative $O_6HMe(NO_2)_2(OAc)_2$ [154°-157°] silky needles

NITRO-DI IMIDO-HYDROQUINONE

C₂H(NO₂)(NH)₂(OH)₂(3 5 2 4 1] Formed from di amido hydroquinone sulphate, HOAc, and HNO, (S G 1 4) (Nietzki a Schmidt, B 22, Needles or prisms. Reduced by SnCl, to 1658) tri amido hydroquinone

NITRO 1MIDO-DI PHENYL-SULPHOXIDE

 $NH < C_0H_1(\overline{NO_2}) > SO$ Formed by nitration of imido di phenyl sulphoxide (Bernthsen, B 17, 2858)

(a)-Di nitro imido-di phenyl sulphoxide

 $NH < C_0H_3(NO_2) > SO$ Formed, together with the (β) -isomeride by nitration of imido di phenyl sulphide (Bernthsen, A 230, 115) Orange needles Reduced by SnCl₂ and HCl to (a) diamido imido di phenyl sulphide Acetyl derivative C₁₂H₅Ac₂N₃SO₈

(β) Di nitro imido-di phenyl sulphoxide Lemon yellow powder Reduced by SnCl2 and HCl to (β) di amido imido di phenyl sulphide

NITRO-DI IMIDO-RESORCIN $C_6H(NH)_2(NO_2)(OH)_2[6\ 4\ 2\ 3\ 1]$ Formed from dı amıdo resorcin sulphate, HOAc, and HNOs (Nietzki a Schmidt, B 22, 1659) Needles K₂A" orange needles

C,H,(NO2)N2 NITRO-INDAZINE [181°] Formed, together with nitro cresol, by heating diazotised (4, 1, 2) nitro o toluidine sulphate with water (Witt, Nolting, a Grandmougin, B 23, 3636) Needles Yields a methyl deriva-Yields a methyl derivative C,H4Me(NO2)N2 [159°], an acetyl derivative [140°], and a bromo derivative C,H,Br(NO2)N2 2290

DI NITRO-INDIN v Indin DI NITRO-INDIGO v INDIGO NITRO INOSITE v INOSITE

NITRO-IODO- compounds v IODO-NITRO-

compounds

NITRO-ISATIN v ISATIN NITRO-ISATOIC ACID v ISATOIC ACID NITRO-LACTIC ACID v NITRO OXY PROPIONIC

TRI-NITRO-LAURENE C₁₁H₁₅(NO₂)₅(?) [84°] From laurene, HNO, and H₂SO₄ (Fittig, A 145,

NITROLIC ACIDS Compounds of the form R CH(NO)(NO₂) or R C(NO₂) NOH They are formed by the action of nitrous acid (ie KNO, and H2SO4) on the sodium derivatives of primary nitro paraffins, and by the action of hydroxyl amine on the compounds $R C(NO_2)Br_2$. Their alkaline solutions are red (V Meyer, B 7, 1510, cf vol 1 p 101) The compounds of the form RR'C(NO)(NO₂) formed by the action of nitrous acid on secondary nitro paraffins are called pseudonitroles. The pseudonitroles are also formed by the action of NO, upon ketones, thus acetone yields $(CH_3)_2C(NO)(NO_2)$ (Scholl, B 21, 506) The pseudonitroles may perhaps 21, 506) The pseudontroles may perhaps be formulated RRC NO NO₂ (V Meyer, B 21, 1291) The pseudontroles do not form salts, their solutions are blue

NITRO-MALONIC ETHER CH(NO2)(CO2Et)2. Formed from malonic ether (1 pt) and HNO, (5 pts of S G 15), the product being extracted with ether (Franchimont a Klobbie, R T C 8 283) Heavy oil, decomposing carbonates and forming a white crystalline compound with NH, decomposing at 150°

Methyl nitro-malonate forms the analogous

CH(NO₂)(CO₂Me),NH₂ [c 166°] o NITRO-MANDELIC ACID C₂H,NO₃ C.H.(NO.) CH(OH) CO.H [140°] Formed from di a-bromo-o-nitro acetophenone and very dilute KOH (Engler a Wöhrle, B 20, 2201) Formed

also from o nitro benzoic aldehyde, KCy, MeOH, and HCl (Engler a Zielke, B 22, 207) crystals, v sol water

Methylether MeA' [745°] Sol alcohol m Nitro mandelic acid [120°] Formed from m nitro a amido phenyl acetic acid and HNO (Plochl a Loe, B 18, 1181) and also from di ω bromo m nitro acetophenone and dilute KOH (E a W) Yellowish rhombohedra with bitter taste -NH,A' - AgA'

Ethyl ether EtA' $[63^{\circ}]$

m Nitro mandelic imido ether C₆H₄(NO₂) CH(OH) C(NH)OEt [84°] Formed from m nitro-benzoic aldehyde, KCy, alcohol, and HCl (Beyer, J pr [2] 31, 393) Dendrition needles (from ligroin) — B'HCl [129°] Needles Dendritic Cold dilute HClAq converts it quickly into m nitro mandelic ether [63°]

p Nitro mandelic acid [126°] Formed in like manner (E a Z) Yields p oxy phenyl glyoxylic acid on boiling with aqueous Na₂CO,

[87°] [76°] Methylether MeA Prisms Ethylether EtA' Needles.

NITRO-MESIDINE v NITRO AMIDO MESITYL-

NITRO-MESITOL C₆HMe₃(NO₂)(OH) [64°] From nitro amido mesitylene and HNO2 (Knecht, Yellow plates (from B 15, 1376, A 215, 98) water), volatile with steam

NITRO-MESITYLENE C₆H₂Me₃(NO₂) [42°] (255°) Formed, together with much di-nitro mesitylene, from mesitylene and HNO₃ (S G 1 38) (Fittig, A 141, 132, 147, 2) Formed also from nitro amido mesitylene and HNO, (Ladenburg, A 179, 170, Klobbie, R T C 6, 31) Triclinic prisms (from alcohol) CrO₂ in HOAc oxidises it to C₆H₂Me₂(NO₂) CO₂H[6 2 1 4] [200°-225°] (Emerson, Am 8, 268)

Di-nitro mesitylene C₆HMe₃(NO₂)₂ Obtained by dropping mesitylene into cooled fuming HNO. Trimetric prisms, m sol hot fuming HNO, alcohol

Tri-nitro-mesitylene C₆Me₃(NO₂)₈ Formed from mesitylene, HNO3, and H2SO4 Colourless needles (from hot alcohol) or tri clinic prisms (from acetone) Yields NH, and dı amıdo mesitylene on reduction by tin and **HClAq**

NITRO MESITYLENE SULPHONIC ACID C₉H₁₁NSO₅ ie C₆HMe₃(NO₂)(SO₃H) [131°] S 100 in the cold Formed from mesitylene sulphonic acid and HNO, (Roze, Z [2] 6, 74, A 164, 65) Prisms (containing 1 aq) -KA' aq -BaA', -CuA', Saq -PbA', aq

(a) NITRO-MESITYLENIC ACID C, H, NO. te 'C₈H₂Me₂(NO₂)(CO₂H) [5 3 2 1] [212°] Formed by nitrating mesitylenic acid (Schmitz, ▲ 193, 162) Colourless crystals (from alcohol)

-BaA'₂ 4aq needles, v e sol water Ethyl ether EtA' [64°] Tab Tables

(B) Nitro-mesitylenic acid $C_{e}H_{2}Me_{2}(NO_{2})(CO_{2}H)[5\ 3\ 4\ 1]$ [223°] Found, in small quantity, in preparing the preceding acid (Fittig, A 141, 149, 147, 48, Schmitz) Formed also by oxidising nitro mesitylene $(q \ v)$ monoclinic crystals (from alcohol) Melts at 179° when crystallised from water —BaA', 4aq - BaA'₂2aq -- BaA', 6aq - CaA', 6aq -MgA', 11aq -AgA'

Ethylether EtA' [72°]. Needles.

NITRO-MESITYL-PHTHALIMIDE

 $C_{e}H_{\epsilon} < CO > N C_{e}HMe_{s}(NO_{s})$ [210°] Formed by nitiation of mesityl phthalimide (Eisenberg, B 15, 1018) Prisms, sol alcohol

Di-nitro-mesityl-phthalimide

 $C_6H_4 < CO > N C_6Me_3(NO_2)_2$ [242°] Formed from mesityl phthalimide, HNO,, and H2SO4(E) Needles, sol alcohol

NITRO METHANE CH, NO. (101°) SG 15 11441, 2 11350 MM 1858 (Perkin, C J 55, 687) SV 59 5 (Schiff, Lossen, A 254,73) HFp 18,600 HFv 17,440 (Thom sen, Th) Formed, unaccompanied by methyl nitrite, from MeI and AgNO₂ (V Meyer, A 171, 32) Formed also by heating potassium chloro acetate with potassium nitrite (Kolbe, J pr [2] 5, 427, Preibisch, J pr [2] 7, 480, 8, 316) Heavy oil With alcoholic potash it gives a pp of CH,K NO2(EtOH), the iqueous solution of which is ppd by HgCl₂, the pp being explosive Iron and acetic acid reduce it to methylamine Fuming H₂SO₄ forms hydroxylamine and CO HClAq (S G 114) at 150° forms formic acid and hydroxylamine Benzoic aldehyde yields C₆H₅ CH CH NO₂ (characteristic) (Priebs, A 225, Nitro methane converts dichlorhydrin CH'Cl CH(OH) CH2Cl into di-chloro formin CH,Cl CH(OCHO) CH2Cl (Pfungst, J pr [2] 32, ZnEt2, followed by water, yields methyldı ethyl hydroxylamıne (Bevad, J R 20, 125)

Di nitro-methane Potassium CHK(NO₂)₂ Formed by passing H₂S into a solution of CBrK(NO₂)₂ mixed with ammonia (Vil liers, Bl [2] 41, 282) Yellow explosive crystals

Tri nitro methane CH(NO2) Nitroform [15°] Formed by boiling with water tri nitro and H₂SO₄ on fulminum and (Schischkoff, A 103, 364) White crystals, m sol water Ex plodes when quickly heated Reduced by tin and HCl to hydroxylamine, NH_s, and HCy (V Meyer a Locher, A 180, 172)

Tetra nitro-methane C(NO2)4 Mol w 196 [13°] (126°) Formed from tri nitro methane, cone H₂SO₄, and fuming HNO₃ (Schischkoff, A 119, 248) White crystals, which will not burn

NITRO METHANE TRICARBOXYLIC ETHER C(NO₂)(CO₂Et)₃ Formed from CH(CO₂Et)₃ and HNO₃ (S G 1 52) (Franchimont

8 Klobbie, R T C 9, 220) Oil

NITRO-METHANE DISULPHONIC ACID CH(NO₂)(SO₃H)₂ The salt K₂A", formed by the action of cone H₂SO₃Aq on chloropicrin crystalhses in minute plates, v sl sol cold water (Rathke, A 161, 153, 167, 220)

NITRO METHOXY- compounds v Methyl derivatives of Nitro oxy compounds

NITRO - DI METHYL - AMIDO - BENZENE SULPHONIC ACID C8H10N2SO5 + e C₆H₈(NMe₂)(NO₂) SO₃H Formed together with C₀H₄(NO₂)NMe₂, from C₀H₄(NMe₂)SO₃H and aqueous NaNO₂ (Michler a Walder, B 14, 2176) Yellow crystals (from water) —BaA'₂— CaA

NITRO-TETRA METHYL-DI-AMIDO-BEN ZOPHENONE C₁₇H₁₀N₂O₃ * ¢ NMe₂.C₂H₂(NO₃) CO C₆H₄ NMe₂ [144°] Formed from CO(C,H, NMe,), by nitration (Nathansohn

a Muller, B 22, 1883) Needles (from warm alcohol), sl son ether

Di-nitro di-methyl-amido-benzophenone

C₁₂H₁(NO₂)₂(NMe₂)CO [142°] Obtained from C₆H₁, CO C₆H₄NMe₂ and fuming HNO₃ (Fischer A 206, 88) Nodules (from dilute HOAc)

Tetra-nitro di-methyl-di-amido-benzophenone CO(C₆H₂(NO₂)₂ NMeH)₂ [225°] Formed by boiling its di nitro-derivative with phenol (Van Romburgh, R T C. 6, 252, 365) Plates, v sl sol alcohol

d sol alcono.

Di nitro-derivative

Formed by CO(C₆H₂(NO₂), NMeNO₂)₂ Formed by the action of conc HNO₂ on CO(C₆H₄NMe)₂ or Reuther. B 20, 3296) Yel- $CS(C_6H_4NMe_2)_2$ (R , Batther, B 20, 3296) low crystals, decomposing at about 210°
NITRO - DI - METHYL - AMIDO - PHENOL

Anhydride of the methylo-hydroxide $C_9H_{12}N_2O_2$ se $C_9H_3(NO_2)<_{NMe_2}^O$ from nitro amido phenol, MeI and KOH (Griess, B 13, 647) Yellow crystals—B'HCl aq—

B'HI 2aq —B',H₂PtCl₃ 6aq yellow crystals
Di-nitro-di-methyl-amido phenol C₈H₉N₃O₄ $i c C_6H_2(NO_2)_2NMe_2(OH)$ [195°] Formed from KCy and alcoholic C₀H₁(NO₂)₂NMe₂ at 50° (Lippmann a Fleissner, M 6, 808) Triclinic yellow crystals Converted by boiling KOHAq into dimethylamine and di nitro resorcin [145° -NH₄A' [195°] —KA' —BaA'₂ 1½aq —AgA' red crystalline pp

Tri nitro methyl amido phenol Nitro-de rivative C₈H(NO₂)₃(OH) NMe(NO₂) [188°] Formed by boiling C.H(NO.), NMe(NO.) with water (Van Romburgh, R T C 8, 275) Yellow crystals (from water) Its methyl ether $C_6H(NO_2)_3(OMe)$ $NMe(NO_2)$ [99°] is formed by dissolving $C_6H(NO_2)_4NMe(NO_2)$ in MeOH The ethyl ether $C_6H(NO_2)_3(OEt)$ $NMe(NO_2)$ [98°] is formed in like manner

DI NITRO TETRA METHYL DI p AMIDO DIPHENYL C₆H₃(NO₂)(NMe₂) C₆H₃(NO₂)(NMe₂) [188°] Obtained by nitration (Michler, B 14,

2164, 17, 118) Red needles
DI NITRO DI METHYL - p - AMIDO - DI PHENYLAMINE [4 2 1]

O.H.(NO₂), NH.C.H.NMe, [168°] Formed from C.H.cl(NO₂), and O.H.(NH₂)(NMe₂) (Lellmann a Mack, B 23, 2739) —Orange plates

p NITRO DI METHYL AMIDO DI PHENYL CARBINOL C₆H₄(NO₂) CH(OH) C₆H₄NMe₂, [96°] Formed by boiling p-nitro benzoic aldehyde with di methyl aniline and HClAq (Albrecht,

B 21, 3294) Thin yellow needles

Reactions -1 Dimethylaniline and ZnCl, yield C.H. (NO.) CH(C.H. NMe.) [177°] -2 Boil ing alcoholic potash and zinc-dust form an azo compound [1990] —8 Zinc-dust and HCl reduce it to di methyl-di amido di phenyl carbi nol [165°] and di methyl di amido di-phenylmethane [93°]

Methylo vodide B'MeI [c 175°] o-Nitro tetra - methyl-di-p-amido tri-phenyl

carbinol C₃H₂N₃O₃ to C₃H₄(NO₃) C(OH)(O₆H₄NMe₂), o-Nitro malachte green [163°] Formed by heating dimethyl aniline (3½ pts) with o nitro-benzous aldehyde (1 pt) and ZiCl₂ (1 pt) on the water both and ordered the second content of the second con bath, and oxidising the resulting leuco base with PbO and dilute H.SO. (O Fischer a Schmidt, B. 17, 1890) Small yellow crystals, sol alcohol

m-Nitro-tetra-methyl-di-p amido-tri-phenylearbinol [3 1] $C_6H_4(NO_2)C(OH)(C_6H_4NMe_2)$ Formed by oxidation of m nitro tetra methyl di amido tri phenyl methane (E a O Fischer, B12, 802) -Picrate small green needles

 $p extsf{-Nitro}$ - $extsf{tetra}$ - $extsf{methyl}$ - $extsf{di-amido-tri-phenyl-}$ carbinol Formed like the two preceding iso merides, and also by heating dimethylaniline with BzCl and ZnCl (E a O Fischer, B 12, 800, 14, 2528) Small golden prisms Dyes a splendid green -- Picrate minute needles

NITRO - DI - METHYL - AMIDO - PHENYL

HEXYL KETONE $C_1H_{22}N_2O_3$ 2e $C_6H_4(NO_2)(NMe_2)$ CO C_6H_{13} [65°] Obtained by nitrating $C_6H_4(NMe_2)$ CO C_6H_{13} (Auger, Bl [2] 47, 42) Yellow needles (from alcohol)

o-NITRO - TETRA - METHYL-DI - p - AMIDO-

TRI-PHENYL-METHANE

 $C_eH_4(NO_2)$ $CH(C_eH_4NMe_2)_2$ o Nutro leuco mala chite green [160°] Prepared by heating o nitro benzoic aldehyde with dimethylaniline and ZnCl., (Fischer, B 15, 682, 17, 1889 monoclinic prisms, sl sol alcohol

m - Nitro - tetra - methyl -di-amido-tri-phenylmethane C₆H₄(NO₂) CH(C₆H₄NMe₂)₂ Obtained in the same way from m nitro benzoic aldehyde (E a O Fischer, B 12, 802)

crystals, sl sol alcohol

p Nitro-tetra-methyl di amido tri phenyl methane [177°] Obtained from p nitro benz oic aldehyde, dimethylaniline, and ZnCl2 at 100° (Fischer, B 14, 2526) Golden plates

Methylo-rodide B"Me,I₂ aq [$\overline{220}$ °] Tetra nitro di-methyl di amido di phenyl $\mathbf{CH_2}(\mathbf{C_6H_2}(\mathbf{NO_2})_2\ \mathbf{NMeH})_{\mathbf{2^*}}$ Formed by boiling its di nitro derivative with phenol (Van Romburgh, R T C 7, 233)

Orange crystals, sl sol hot alcohol

Di nitro derivative
CH₂(C₆H₂(NO₂)₂ NMe NO₂)₂ Formed
CH₂(C₆H₄ NMe₂)₂, acetic acid, and HNO₃ Formed from Yellow crystalline substance, decomposing at 217°-220°

Hexa-nitro tetra methyl di amido tri-phenyl methane [200°] Formed by nitrating $CH(C_6H_5)(C_6H_4NMe_2)_2$ (O Fischer, A 206, 122) Golden needles, sol alcohol

NITEO - DI - METHYL - p AMIDO-PHENYL AMIC ETHER C₁₂H₁₅N₅O₅ 1e [134] C.H. (NMe2)(NO2) NH CO CO2Et [152°] Formed from di methyl-amido phenyl oxamic ether and nitrous acid (Wurster a Sendtner, B 12, 1804) Red needles Gives C,H,(NMe,)(NH,), on re duction by tin and HClAq

NITRO - TETRA - METHYL - DI - AMIDO -PHENYL-DI-TOLYL METHANE

 $C_eH_4(NO_2)$ CH(C_eH_2Me NMe₂)₂ [224°] Formed from di methyl m toluidine and p nitro benzoic aldehyde (Kock, B 20, 1562) Yields a picrate [199°]

NITRO METHYL-AMINE & METHYL NITRO **AMINE**, p 279

Nitro-di-methyl-amine v. Dr METHYL NITRO-AMINE, p 280

o-NITRO-METHYL-ANILINE C,HaN2O2 2 6 [12] C.H.(NO.) NHMe [28°] Formed by heating o nitro phenol with alcoholic methylamine

at 180° (Hempel, J pr [2] 41, 164) Nutrosamune C₆H₄(NO₂) N(NO)Me [36°]

m Nitro-methyl-aniline

[1 3]C_sH_s(NO_s).NHMe. [66°]. Formed by methyl-

ation of m nitro aniline (Nölting a Stricker, B. 19, 548) Reddish yellow needles, sol I ot Aq

Acetyl derivative C_aH₄(NO₂) NAcMe. [95°] Needles, sol water (Meldola, C J 53, 777). Benzoyl derivative C,H,BzN.O₂ [105°]

Nitrosamine C₆H₄(NO₂) N(NO)Me [70°]

p Nitro methyl aniline

[1 4]C,H,(NO,) NHMe [152°] Formed by heating [1 4]C H,(NO,) N, NMe C,H,(NO) [4 1] with HClAq (Meldola a Salmon, C J 53,774) Short thick yellowish brown prisms or tablets (from alcohol), sl sol hot water, v sol alcohol

C₆H₄(NO₂) NAcMe Acetyl derivative

[153°]

Benzoyl derivative [112°] Prisms Nitrosamine C, H, (NO,) N(NO)Me [100°]

m Nitro di methyl-aniline $C_6H_4(NO_2)$ NMe₂[1 3] [61°] (280°-285°) Large red prisms Obtained by heating m nitro aniline hydrobromide (1 mol) with MeOH (2 mols) at 100° (S a B) Prepared by nitra tion of dimethylaniline in presence of a large excess of H₂SO₄, p nitro dimethylaniline being formed in smaller quantity A mixture of 193 g of HNO₄ (S G 1 35) and 600 g of ordinary H₂SO₄ is allowed to slowly drop into a solution of 200 g of dimethylaniline in 4,000 g of ordinary H₂SO₄, keeping the mixture cooled below 5° After standing for 4 or 5 hours at a After standing for 4 or 5 hours it is poured into about 10 litres of iced water and filtered from the ppd p nitro derivative, more of which separates on partial neutralisation with Na₂CO₄ (50 or 60 g on the whole) The filtrate neutralised with Na₂CO₃ deposits the m nitro di methyl aniline, the yield is 160 to 170 g (Groll, B 19, 198)

Methylo bromide C₆H₄(NO₂) NMe₅Br Crystalline (Stadel a Bauer, B 19, 1941) Yields crystalline B'MeCl, B', Me PtCl, and unstable B'MeOH which is converted by m nitro phenol

into $C_6H_4(NO_2)$ NMe₃ O $C_6H_4(NO_2)$ [62°] p Nitro di methyl aniline $C_0H_4(NO_2)$ NMe₂ [163°] Formed by adding HNO, to a solution of dimethylaniline in HOAc (Weber, B 10,760) Formed also by oxidising p nitioso di methylaniline with KMnO₄ (Wurster, B 12, 528, cf Schraube, B 8, 616), by heating p chloro nitro benzene with NMe, at 180° (Leymann, B 15, 1234), and by the action of nitrous acid on C_cH₄(NMe₂) SO₃H (Michler a Walder, B 14, 2176), on C₆H₄(NMe₂) N₂ C₆H₄NMe (Lippmann a Fleissner, B 16, 1421), and on the base C₆H₃(NO₂)(NH₂)NMe (Hewi, B21, 2309) Yellow needles Does not form salts

Di nitro-methyl aniline C,H N₃O₄

 $C_6H_3(NO_2)_2$ NHMe [177°

Formation —1 From chloro di nitro benzene and methylamine (Leymann, B 15, 1234) -2By heating C₆H₄(NO₂) NMe, [78°] in HOAc with bromine (L), or CrO, (Van Romburgh, R T C 8, 250)—3 By nitrating the formyl, acetyl, or oxalyl derivative of methyl aniline (Norton a Allen, B 18, 1995, Norton a Livermore, B 20, 2273)

Properties —Yellow crystals, v sol alcohol,

sl sol hot water

Dı nıtro dı-methyl-aniline

 $C_6H_3(NO_2)_2 NMe_2[4\ 2\ 1]$ [87°] Formed from $C_0H_3Cl(NO_2)_2$ and NMe₃ (Leymann, B 15, 1283) Prepared by slowly adding 500 g of dimethyl aniline to a mixture of 6 litres of ordinary cone. HNO, and 6 litres of water, cooled to 0° , the yield being 116° (Mertens, B 19, 2123, cf Weber, B 10, 763) Large yellow pointed crystals or prisms V sol alcohol, chloroform, benzene, acetic acid, and HClAq Heated with 10 pc KOH aq it readily decomposes into dinitro phenol [114°] and dimethylamine Boiled with fuming HNO, it is converted into tri nitro phenyl methyl nitramide $C_{\rm e}H_{\rm e}(NO_{\rm e})_{\rm s}$ NMe(NO₂)

Salts —B'HCl unstable —B'₂H₂Cl PtCl granular pp, or large brownish red pyramids

Di nitro di methyl aniline
C,H,(NO), NMe [5 3 1?] Formed by nitration
of dimethylaniline with dilute HNO, (equal vols
of HNO₃ (S G 1 4) and water) without cooling,
the yield being 15 pc (Mertens, B 19, 2125)
Golden brown plates Decomposes at 250°-272°
Soluble in phenol It is attacked only by very
strong KOH Boiled with fuming HNO₃ it is
converted into di nitro phenyl methyl intramine
C,H,(NO), NMe(NO₃), a crystalline body which
explodes above 220°

Tri-nitro methyl-aniline $C_2H_0N_4O_6$ is C_6H (NO₂), HM4e [111°] Formed from C II $Cl(NO_2)_s$ (pierry lehloride) and methylamine in hot alcoholic solution (Van Romburgh, R T C 2, 31, 105, 305) Yellow needles (from alcohol) Gives off NMeH₂ when heated with

KOHAq

Nitro derivative C_aH (NO₂)₃NMe(NO₂) [127°] Obtained from dimethylaniline (10 pts), H SO₄ (100 pts), and HNO₃ (200 pts of S G 1 48) Obtained also from methyl aniline and HNO₃ (Romburgh), and by nitration of dimethyl amido phenyl naphthyl sulphone (Michler a Schacht, B 12, 1790) Pale yellow crystals (from alcohol) Yields pieric acid on boiling with aqueous Na CO₃ Reduced by tin and HClAq to tin amido phenol

Tri nitro-di-methyl aniline C₀H (NO₂)₃NMe₂ [138°] Formed from picryl chloride and alco holic dimethylamine (Van Romburgh, R T C 2, 105, 8, 250) Yellow crystuls (from benzene) Forms with picric acid the crystalline compound

C₈H₈N₄O₆C₇H (NO)₇OH [114⁵]

Tetra-nitro-methyl-aniline Nitro diri vative C₂H(NO₂), NMe(NO) [146°] Formed from the preceding tri nitro di methyl aniline and HNO₃ (S G 1.5) (Van Romburgh, R. T. C. 8, 274) Yellowish white needles On dissolving in MeOH it yields C₂H(NO₃)₃(OMe) NMe(NO₂) [99°], alcohol forms C₄H(NO₃)₄(OEt) NMe(NO₂) [98°] in like manner Aquicous methylamine produces C₄H(NO₃)₄(NMeH), [235°] If a few diops of aniline be poured upon the nitro derivative it catches fire

NITRO-METHYL-ANTHRAQUINONE

 $C_1, H_eO_s(CH_s)(NO_2)$ [270°] Prepared by nitration of methyl anthraquinone by adding KNO_s to its solution in H_2SO_s (Romer a Link, B 16, 696) Sublimes in small white needles SI solution and ether, v sol introbenzene

TRI-NITRO-TRI-METHYL-BENZENE $C_8Me_8(NO_2)_8$ [1 2 3 4 5 6] [209°] Got by nitration (Jacobsen, B 19, 2517)

NITRO-METHYL-BENZOIC ACID v Nitro toluic acid

Nitro di-methyl benzoic acid C₂H₂NO₄ ie C₂H₂Me₂(NO₂) CO₂H [195°] Formed by oxi

dising nitro ψ cumene (Schaper, Z 1867, 13) Slender needles —CaA'₂6aq —BaA'₂9aq —EtA' p-NITRO-METHYL COUMARILIC ACID

 $C_{e}H_{s}(NO_{2}) < \frac{CMe C CO_{2}H}{O}$ [178°] Obtained by

saponification of its ethyl ether, which is formed by heating dry p-nitro phenolsodium with chloro-acetic ether and dissolving the product (probably p nitro phenoxy acetic ether) in conc H₂SO₄ (Nuth, B 20, 1332) Short yellow needles M sol hot water, alcohol, and ether, nearly insol cold water Most of the salts are sparingly soluble—AgA ½aq small needles

Ethyl ether EtA' [74°] White needles

Ethyl ether EtA' [74°] White needles NITRO - METHYL ETHYL - BENZENE v

NITRO ETHYL TOLUENE

NITRO $(B\ 2\ Py\ 2)$ DIMETHYL $(Py\ 3)$ ETHYL QUINOLINE $C_{13}H_{14}N(NO_s)$ [109°] Formed by mitration of di methyl ethyl quinol ine (Harz, $B\ 18,\ 3391)$ Triclinic crystals Easily soluble in chloroform, m sol ether

Salts — B'HCl* easily soluble yellow crystals — B'₂H PtCl₆2aq short thick orange

crystals, sol hot water

Nitro (B 2, 4, Py 2) tri methyl-(Py 3) ethyl quinoline $C_{14}H_{16}(NO_2)N$ [90°] Formed by nitration of the base (cf p 326) Needles (from alcohol) It is accompanied by the dinitro derivative $C_{14}H_{16}(NO_2)_2N$ [1525°] Waldbott, B 23, 2272)

DI NITRO METHYLIC ACID (so called) CH, N, O, 2 & CH, NH NO,? By passing NO into Zn Me there is formed CH, (ZnMe) N, O,, which is decomposed by water yielding CH, (ZnOH)N, O, whence CO, yields crystalline (CH, NO), Znaq, which is converted, by adding Na, CO, to its aqueous solution, into very soluble CH, NaN, 2O, 2aq (Frankland, CJ 11, 88)

DI NITRO METHYL MESIDINE Nutramine $C_8Me_1(NO_1)$, $NMe(NO_1)$ [138°] Formed from $C_9Me_1H_1$, NMe, H_2SO_4 , and HNO_2 (Klobbie, R T C O, 31) Crystals, al sol ether

NITRO METHYL NAPHTHALENE

C₁₁H₄NO₂ [81°] Formed, together with the di nitro derivative [200°], by nitration of (8) methyl naphthalene (Schulze, B 17,844) Thin yellowish needles

DI NITRO $(Py\ 3)$ METHYL- (β) NAPHTHO QUINOLINE $C_{11}H_1(NO)_2N$ Four bodies of this constitution, melting at 227° , 230° , 205° - 212° , and 250° , may be obtained, as well as a tetra nitro derivative $[277^\circ]$, by intrating the $(Py\ 3)$ methyl (β) naphthoquinoline which is formed by condensation of (β) naphthylamine with paral dehyde $(\text{Seit}_2, B\ 22, 256)$

NITRO DI METHYL PHENYL ACETIC

ACID [3 5 2 1] C₄H₂(CH₂),(NO₂) CH₂ CO₂H

Nutro mesityl acetic acid [139°] Formed by
heating (5 3 1) di methyl phenyl acetic acid with
dilute nitric acid (Wispek, B 16, 1579) Long
fine needles Sol alcohol, ether, and hot water,
msol cold water On reduction it gives carbo

mesyl $(C_6H_2(CH_8)_2 < \frac{CH}{NH} > CO)$

Salts — A'₂Ca4aq thick needles — A'₂Ba4₃aq fine needles — A'Ag
Di-nitro-methyl phenyl acetic acid v Dr.
NYRO TOLYL AGETIC ACID.

(B 4) NITRO-(Py 8) METHYL QUINOLINE o - Nitro quinaldine [137°] Formed, together with the ssomeride [82°] by nitration of $(Py\ 3)$ methyl quinoline (Doebner a Miller, B 17, 1699, Gerdeissen, B 22, 245) Formed also by the action of aldehyde on m nitro aniline Long needles, sl sol cold water -- B HCl prisms - B'2H2PtCl

(B 1 or 3) Nitro (Py 3)-methyl-quinoline C.H.Me(NO,)N m Nitro quinaldine Formed as above, and also by the action of aldehyde on m nitro aniline (D a M) Slender needles, volatile with steam - B'HCl

small needles

B'₂H₂PtCl₆ needles
(B 1 or 3) Nitro-(B 2) methyl-quinoline Formed by nitrating (B 2) methyl quinoline (Noelling a Trautmann, B 23, 3655)
Formed also from (2, 1, 4) intro toluidine, gly
cerin, pieric acid, and H₂SO₄ Needles Yieldi Yıelds

a methylo rodide [190°]
(B 4) Nitro-(B 2) methyl-quinoline
ÇMe CH——C CH ÇH
[199°] Forme $[122^{\circ}]$ Formed from CH C(NO₂) C N CHnitro p toluidine (N a T) Yellow needles

 $(\vec{B} \ 1) \ \text{Nitro-}(\grave{B} \ 4) \ \text{methyl-quinoline}$ CH C(NO₂) C CH CH $[93^{\circ}]$ Formed from CH CMe CN CH 4, 2, 1)-nitro-o toluidine and also by nitrating (B 4) methyl quinoline

Nitro-methyl-quinoline [127°] Got by nitrating lepidine (Busch a Konigs, B 23, 2687)

Nitro- $(\hat{P}y$ 3) methyl quinoline tetrahydride $Netroso derivative C_{10}H_{11}(NO_2)N NO [152°]$ A product of the action of nitrous acid on (Py 3)methyl quinoline tetrahydride (Möller, À 242, Golden plates (from alcohol benzene)

Nitro $(Py \hat{4})$ methyl-quinoline tetrahydride O₆H₃(NO₂) CH, CH₂ NMe CH₂ Netro karroline Formed by careful nitration of kairoline (Feei a Königs, B. 18, 2390) Long ied needles

(B 1) Nitro (B 2, 4) di methyl quinoline CMè C(ŃO₂) C CH CH CH CMe ČN CH [108°] Formed by CH CMe nitrating di methyl quinoline, and also from nitro m-xylidine [125°], glycerin, H₂SO₄, and pieric acid (N a T) Yellow needles

Nitro-(B 2, 4, Py 3)-tri methyl quinoline CMe CH CH CH [92°] Formed by nitro $[92^{\circ}]$ Formed by nitra CH CMeC N CMe ting tri methyl quinoline (Panajotoff, B 20, 35) Needles -B'2H2PtCl3daq crystalline

D1 - nitro - (Py - 4) - methyl - quinoline tetrahydride C₆H₂(NO₂)₂ CH₂ CH₂ NMe CH₂ karroline [148°] Formed from kairoline, HOAc,

and HNO, (Feer a Königs, B 18, 2390) Golden

yellow plates, sol alcohol

DI - NITRO - DI - METHYL - SULPHAMIDE C₂H_eN₄SO₆ i e SO₂(NMe NO₂)₂ [90°] Formed from di methyl sulphamide and HNO₃ (Franchi mont, R T C 8, 419) Crystals (from benzene)

NITRO - METHYL - THIENYL METHYL KETONE C,H,NSO, te C,MeH(NO2)S CO CH, Obtained by nitrating C, MeH, S CO CH, (Demuth, B 19, 1861) Needles (from ether)

NITRO DI METHYL-THIOPHENE C.H. NSO, s.e. SC, Me2H(NO2). Netro throxens

Oil, formed from di methyl thiophene vapour,

HOAc, and HNO_s (Messinger, B 18, 1638) NITRO METHYL-o-TOLUIDINE C₈H₁₀N₂O te C₆H₃Me(NO₂) NHMe [2 4 1] [134°] Obtair ed by exidation from nitrose methyl e toluidine C₆H₃Me(NO) NHMe (Kock, A 243, 309) Green ish yellow needles, sol benzene

Nitro-methyl p toluidine

C₆H₃Me(NO₂) NHMe [4 2 1] [85°] Formed from nitro-p toluidine and MeI (Gattermann, B 18, 1487, Niementowski, B 20, 1874) Red needles (from alcohol) or tables (from benzene)

(250-255° at Acetyl derivative [64°] 270 mm) Plates $-B'C_8H_2(NO_2)_3OH$ $[212^{\circ}]$

Di-nitro-methyl-o-toluidine Nitro deriva- $[2\ 4\ 6\ 1]$ C₆H₂Me(NO₂)₂NMe NO₂ [120°] Formed from di methyl o toluidine and HNO, (Van Romburgh, R T C 3, 395) Pale yellow crystals Potash converts it into methylamine and di nitro o cresol

 ${f Di-nitro-methyl-}p$ toluidine

 $C_6H_2Me(NO_2)_1NHMe[4 6 2 1]$ [129°] Obtained from C, H, Me(NAcMe) and HNO3 (A L Thomsen, B 10, 1582, Gattermann, B 18, 1487) Red needles (from dilute alcohol)

C₆H₂Me(NO₂)₂ NMe NO Nitrosamine

[125] Yellow needles

Nitro derivative C₆H₂Me(NO₂), NMe NO₂ [139°] Formed from di methyl-p toluidine (1 pt), H₂SO₄ (2 pts), and HNO₃ (10 pts) (Van Romburgh, R T C 3, 404) The same compound [130°] appears to be formed by the action of dilute HNO, on [14]C,H,Me NAcMe (Norton a Livermore, B 20, 2268) Nearly colourless Nearly colourless crystals (from boiling alcohol) Yields di nitro p cresol on boiling with potash

Tri nitro-methyl m toluidine Nitro-de [3 6 4 2 1] C, HM (NO), NMe NO rivative [102°] Formed from di methyl m toluidine and HNO₃ (S G 15) (Van Romburgh, R T C 3, 413) Pale yellow crystals

Tri nitro methyl p toluidine

C₆HMe(NO₂), NHMe [4 6 3 2 1] [138°] Formed by further nitration of nitro methyl p toluidine Yellowish crystals

Nitro di-methyl m toluidine

 $C_6H_8Me(NO_2)$ NMe₂ [84°] Obtained by oxidising nitroso dimethyl m toluidine with KMnO₄ (Wurster a Riedel, B 12, 1800) Yellow needles

Di nitro di methyl-m toluidine C_cH₂Me(NO₂), NMe₂ [107°] Prepared by nutration of dimethyl *m* toluidine dissolved in HOAc (W a R) Yellow needles

Di nitro di-methyl m toluidine

 $C_6H_2Me(NO_2)_2$ NMe₂ [168°] Formed from dimethyl-m toluidine, HNO₃ and H_2SO_4 (W a R) Less sol alcohol than the isomeride [107°]

(a) NITRO NAPHTHALENE C₁₀H₇NO₂ Mol w 173 [56°] (Mills, P M [5] 14, 27), [61°] (D'Aguiar, B 5, 370, Schiff) (304°) (De Coninck, B 5, 12) S V S 141 (Schiff, A 223, 265) S G ± 1331 (Schröder, B 12, 1613) S (88 p c alcohol) 28 Formed by nitration of naph thalene (Laurent, A Ch [2] 59, 378, Beilstein a Kuhlberg, A 169, 88, Guaresch, B 10, 294) Formed also by elimination of NH_2 from (a) nitro (a)-naphthylamine (Liebermann, A 183, 235)

Preparation -By shaking naphthalene with nitric acid in the cold, and recrystallising from alcohol or ligroin (B a K , cf Piria, A 78, 32) Prepared also by stirring naphthalene (250 pts.) with a mixture of HNO₃ (200 pts) and H₂SO₄ (800 pts) at 40°-50° (Witt, Chem Ind 10, 215)

Properties — Pale yellow prisms A few milligrammes projected into a red hot test tube containing nitrogen detonates slightly with a white flame, a larger quantity gives a red flame, with a still larger quantity no flame is seen

(Berthelot, A Ch [6] 16, 24)

Reactions—1 Readily reduced to (a) naph thylamine Zinc dust and HClAq yields chlorinated naphthylamines—2 PCl, forms (a) chloro naphthalene—3 Chlorine yields mono-, di, tri, and tetra chloro naphthalenes (Atterberg, B 9, 316, 926)—4 Bromine forms bromo nitro naph thalene [122 5°], di bromo-nitro naphthalene [98°], and two tetrabromides—6 HBrAq at 195° yields CloH,Brand CloH,Br. (Baumhauer, R 4, 926)—6 CrO, in HOAc forms c-nitro phthalic acid (Beilstein a Kurbatoff, C C 1881, 359)—7 Distillation over senc dust produces (ab) naphthazine (G Schultz, B 17, 478)

thazine (G. Schultz, B. 11, 210)

Tetrabromide C₁₀H₁(NO)|Br₁ [131°] S
(935 pc alcohol) 26 at 152° Formed from
mitro naphthalene and bromine (Guareschi, A
222, 286) White needles When kept at 137°
in a current of air for some time it changes to an
isomeride [148°] and C₁₀H₂Br(NO), [122 5°]
When boiled with alcohol for a long time it
changes to a second isomeride [173°], S (935°)

pc alcohol) 13 at 152°

(β) Nitro naphthalene C₁₀H₂NO₂ [79°] Formed by eliminating NH₂ from (2, 1) intro (α) naphthylamine (Lellmann, B 19, 236, 20, 891) Formed also by the action of precipitated Cu₂O (2 mols) upon a solution of (β) diazonaphthalene nitrite (1 mol) obtained by adding a solution of 12 g NaNO₂ in 40 g water to amixture of 7 g of (β) naphthylamine, 15 g HNO₃, and 250 c c of water The yield is small (Sandmeyer, B 20, 1496) Yellow needles, v sol alcohol Volatile with steam Reduced by zinc and HOAc to (β) naphthylamine

"a" Di-nitro-naphthalene C₁₀H₆(NO_{.)2} [14] Mol w 218 [212°] Formed, together with the (1,1') isomeride, by boiling naphthalene with fuming HNO₃ or by heating it with HNO₄ and HSO₄ at 100° (Darmstadter a Wichelhaus, B 5, 253, D'Aguiar, B 5, 370, Beilstein a Kurbatoff, A 202, 219) Formed also by heating nitro (a) naphthoic and [239°] with HNO₄ (S G

13) (Ekstrand, B 18, 2881)

Properties—Six sided needles (from HOAc), v sl sol HOAc A few milligrammes thrown into a red hot tube full of nitrogen detonate with reddish white flame (Berthelot, A Ch [6]

Reactions—1 Oxidised by HNO₃ (S G 115) at 150° to c mtrophthalic, s di mtro benzoic, and pierre acids (Bellstein a Kurbatoff, Bl [2] 34, 327)—2 POl₃ yields (γ)-di-chloro naph-

thalene [107°]

'β' Di-nitro-naphthalene C₁₀H_s(NO₂)₂ [1 1']
[172°] S (88 pc alcohol) 187 at 19° S
(benzene) 72 at 19° S (chloroform) 1 at 19°
Formed, at the same time as the preceding, by nitrating naphthalene (Darmstadter a Wichelhaus, A 152, 301, Beilstein a Kuhlberg, A 169, 86) Formed also by heating nitro (a) naphthoic acid [215°] with HNO₂ (S G 1 3) (Ekstrand, B 18, 2881), and by eliminating NH₂ from di-nitro (β)-naphthylamine (Gaess, J. pr

[2] 43, 37) Tables, more soluble in HOAc, chloroform, benzene, and acetone than the (1,4')someride

Reactions —1 Dilute HNO, at 150° yields di nitro phthalio acid [226°], s di nitro benzoic acid, and picrio acids —2 PCl, forms \(\) di chloro-naphthalene and \(\) tri chloro naphthalene.

(γ) Di-nitro-naphthalene C₁₀H_e(NO₂) [1 d] [144°] Obtained from di mitro (a)-naphthyl amine [235°] by elimination of NH₂ (Liebermann a Hammerschlag, A 183, 272) Yellow needles

(5) Di-nitro-naphthalene C₁₀H_a(NO₂)₂ [1 3'?] [162°] Formed by eliminating NH₂ from dinitro-(β) naphthylamine[238°] (Graebe a Drews, B 17, 1172) Yellow needles, v sol alcohol 'a'-Tri-nitro-naphthalene C₁₀H_a(NO₂)₃ Mol

'a'-Tri-nitro-naphthalene C₁₀H₅(NO₂), Mol w 263 [122°] Formed by further nitration of 'a'-di nitro naphthalene (D'Aguiar, B 5, 372,

897) Monoclinic crystals, v sol HOAc

'β'-Trı-nitro-naphthalene C₁₀H₃(NO₂)₄ [213°] S (88 pc alcohol) 06 at 23° Ob tamed by further nitration of 'β' di mitro naphthalene (Laurent, A 41, 98, D'Aguiar, Beilstein a Kuhlberg, A 169, 96) Formed also by eliminating NH, from tri nitro (a) or (β)-naphthylamine (Staedel, B 14, 901, A 217, 174), and by the action of fuming HNO, and cone H₂SO, on nitro (a) naphthoic acid (Ekstrand, B 19 1131) Prisms (from HOAc), v sl sol HOAc and ether

(7) Tri-nitro-naphthalene $C_{10}H_5(NO_2)_3$ [147°] (B a K), [154°] (A.) S (90 p c alcohol) 11 at 185° S (ether) 38 S (benzene) 105 at 185° Obtained by boiling 'a' di nitro naphthalene for a few minutes with H_2SO_4 and fuming HNO₃ (Beilstein a Kuhlberg, B 6, 647) Yellow plates

plates

'a'.Tetra - nitro - naphthalene C_{1e}H₄(NO₂)₄ [259°] Formed by boiling 'a' di nitro-naph thalene with HNO₂ and H₂SO₄ for some hours (A, B a K) Crystals (from chloroform), almost insol alcohol

' β ' Tetra - nitro - naphthalene $C_{10}H_4(NO_2)_4$ [200°] Formed by heating ' β ' di nitro naphthalene with fuming HNO₃ for 4 days at 100° (Lautemann a D'Aguiar, Bl 3,261) Asbestoslike needles (from alcohol) Explodes when heated

References — Bromo, Chlobo-, and Iodo-, NITRO NAPHTHALENE

NITRO-NAPHTHALENE DICARBOXYLIC ACID C₁₀H₅(NO₂)(CO_.H). Nutro naphthalic acid Got by oxidising intro acenaphthene (Quincke B 21, 1454) Yellow needles On heating it yields an anhydride [220°]—CaA″aq—(NH_.)₂A″aq 'a'-NITRO-NAPHTHALENE SULPHONIC

"a'-NITRO-NAPHTHALENE SULPHONIC ACID C,0He(NO2)(SO₃H) [14'] Formed from (a) nitro naphthalene and fuming H₂SO₄ or CISO,H (Laurent, C R 31, 537, Armstrong a. Williamson, C J Proc 2, 233, Erdmann, A 247, 311) Formed also by nitrating naphthalene (a)-sulphonic acid (Cleve, Bl [2] 24, 506). Straw yellow prisms (containing 4aq), v sol. water, sl sol dilute H₂SO₄. Tastes bitter Its K salt distilled with K₂Cr₂O₇ and HCl gives chloro nitro-naphthalene [111°] and di chloronitro naphthalene [85°] Sodium amalgam reduces it to (a) naphthylamine and H₂SO₄ (Claus Granff, R 10, 1308)

a Graeff, B 10, 1303)
Salts — KA' ½aq S 2 1 at 15° — NH, A' 1½aq
— NaA' ½aq — MgA', 3aq. — CaA', 2aq. — BaA', 3aq.

— ZnA',6aq — PbA',3aq — MnA',2aq -CuA',24aq — AgA' monoclinic prisms Ethyl ether EtA' [101°]

Chloride C10H6(NO2)(SO2Cl) [113°].

 $Amide C_{10}H_{e}(NO_{2})(SO_{2}NH_{2})$ Nitro-naphthalene-'B' sulphonic acid

C10H6(NO2)(SO3H)[1 3'] Formed, together with two or more isomerides, by nitration of naph thalene (B)-sulphonic acid (Cleve, Bl [2] 26, 444), and, together with a larger quantity of the ' α ' acid and some of the θ acid by heating mtro naphthalene with H,SO, containing excess of SO₃ at 100° (Palmaer, B 21, 3260) Yields O10H6Cl2 [48°]

Salts — KA' — NH, A' — NaA'3aq — BaA'2aq S 115at22° — MgA'27aq — CaA'2aq — ZnA'26aq --PbA'23aq — MnA'26aq — CuA', 6aq — AgA'

Ethylether EtA' [115°]

Chloride C10H6(NO2) SO2CI [126°] Monoclinic crystals, $\vec{a} \ \vec{b} \ \vec{c} = 996 \ 1^{\circ} 831$, $\beta = 81^{\circ} 28'$ Amide [184°] Yellowish needles

(γ)-Nitro-naphthalene sulphonic acid

C₁₀H₆(NO₂)(SO₃H)[1 3] Formed, together with the ' β ' and (θ) isomerides, by nitration of naph thalene (3) sulphonic acid (Cleve, B 19, 2170) thatele (3) suphonic sent (cote, b 1s, 21°0).

Its chloride on heating with PCl, yields Cl₀H₆Cl₂

[61°] — KA' — NaA' — BaA', 3aq — PbA', 3aq

Ethyl ether EtA' [115°]

Chloride Cl₀H₆(NO₂) SO₂Cl [140°]

Amide [225°] Long needles

(θ) Nitro-naphthalene sulphonic acid $C_{10}H_6(NO_2)(SO_3H)$ [1 2'] The Ba salt is the most soluble of the Ba salts of the acids obtained by nitration of naphthalene (β) sulphonic acid (Cleve, BI [2] 29, 415, B 21, 3264) Occurs also among the products of sulphonation of (a) nitro naphthalene (Palmaer) Its chloride, | National | National

Ethylether EtA' [107°] Needles Chloride [167°] Yellow needles Amide [223°] Needles

Nitro naphthalene sulphonic acid

C₁₀H_s(NO₂)(SO₃H)[1 4] Formed, together with the (11') and 14') isomerides by nitration of naphthalene (a) sulphonic acid, the acids being separated by crystallisation of their chlorides from benzene (Cleve, B 23, 958) Yellowish crystalline mass —KA'—NaA'aq—CaA'₂2aq S 2 7 at 17°, 7 at 100°—BaA'₂aq S 1 5 in the cold, 3 at 100°—PbA'₂6aq—AgA' needles

Methyl ether MeA' [117°] Ethyl ether EtA' [93° Chloride C₁₀H₆(NO₂)SO₂Cl Amide [188°] Octahedra $[99^{\circ}]$

Nitro naphthalene sulphonic acid

C₁₀H₆(NO₂)(SO₃H) [1 1'] A product of the nitration of naphthalene (a) sulphonic acid (Cleve, B28, 962)

Chloride [101°]

'a' Nitro naphthalene disulphonic $C_{10}H_{1}(NO_{2})(SO_{3}H)_{2}[4\ 2\ 2']$ Obtained from its chloride, which is formed by nitrating naphthalene 'a' disulphone chloride C₁₀H₆(SO₂Cl)₂ (Alén, Bl [2] 39, 63, Bn 2, 156) Needles, v e. sol water —Na₂A"6aq —K₂A"3aq —CaA"5aq -BaA" 5aq -PbA" 4aq -Ag,A" 3aq

Chloride C₁₀H₅(NO₂)(SO₂Cl), [141°] With PCl, it yields θ-tri chloro naphthalene

[287°] Amrde

'B' Nitro naphthalene disulphonic $\mathbf{C}_{10}\mathbf{H}_{5}(\mathrm{NO}_{2})(\mathrm{SO}_{3}\mathbf{H})_{2}[1\ 3\ 2']$ Formed by nitrating naphthalene 'B' disulphonicacid (Alén) Scales -Na₂A" 2aq -K₂A" -CaA" 2aq -BaA" 2aq -PbA" 2aq -Ag₂A" 2aq

Chloride $C_{10}H_5(NO_2)(SO_2Cl)_2$ With PCl_s it gives (γ) tri chloro naphthalene

Amide [above 300°] Needles

Di nitro naphthalene 'a'-disulphonic acid $\begin{array}{cccc} C_{10}H_4(NO_2)_2(SO_3H)_2 & Obtained from its chloride\\ which is formed by nitrating naphthalene\\ `a' disulphonic acid (Alén) — <math>K_2A''$ — K_2A'' 4aq -BaA" 5aq -Ag₂A" aq Chloride [219°] Needles (from benzene)

Amide C₁₀H₄(NO₂)₂(SO₂NH₂) [c Peri NITBO (a) NAPHTHOIC ACID

 $\begin{array}{cccc} C_{10}H_6(NO_2)(CO~H)[1~1'] & [215^\circ] & S & 04~in~the\\ cold & S & (alcohol)~5 & Formed, & together with \end{array}$ the (1,4')-isomeride by nitrating (a) napththoic acid (Kuchenmeister, B 3, 739, Ekstrand, B12, 1393, 18, 73, 2881, 19, 1138, J pr [2] 38, 156, 276) Prisms, v sol alcohol Yields on nitration di nitro naphthalene [170°]

Salts -NaA' -CaA' 3aq S 2 at 15° -

 $\begin{array}{lll} \textbf{BaA'}_2 6aq & -\text{PbA'}_2 aq & \text{yellow prisms} \\ & & Ethyl \ ether \ \text{EtA'} & [69^\circ] & \text{Octahedra} \\ & & \textit{A mide} \ C_{10} \text{H}_{_0} \text{(NO)(CONH)} \ [280^\circ] & \text{Needles,} \end{array}$ converted by conc HClAq at 170 into

Nitro (a) naphthoic acid

 $C_{10}H_{e}(NO_{2})(CO_{2}H)[1 \ 4']$ S (alcohol) 5 at 15° [239°] 8 02 at 15° Formed as above, and also by saponifying its nitrile which is obtained by nitrating the nitrile of (a) naphthoic acid Graeff, B 14, 1063, 16, 2250, F-kstrand, J pr [2] 38, 241) Needles HNO, (S G 1 3) converts it into di nitro naphthalene [212°] —NaA' 5aq —CaA', 2aq S 63 at 15°—BaA', 3\frac{1}{2}aq yellow needles -PbA'251aq

Methyl ether MeA' [110°] Ethyl ether EtA' [93°] Isopropyl ether PrA' [101°] Nitrile C10H6(NO2)CN [205°]

(γ) Nitro (α)-naphthoic acid [255°] by heating its nitrile with HClAq at 160° (Graeff, B 16, 2252) Needles (by sublimation)
Nitrile [153°] Formed, together with the

Nitrile [153°] isomeride [205°] by nitrating (a) naphthonitrile 'a'-Nitro (8) naphthoic acid [220°] Formed,

as well as the four following acids, by nitration of (8) naphthoic acid (Ekstrand, B 12, 1325) Needles — CaA'₂ S 26 at 15° $Ethyl\ ether\ EtA'$ [82°] Needles

'β' Nitro (β) naphthoic acid

 $C_{10}H_6(NO_2)(CO_2H)[1'or4'2]$ [293°] Formed as above (Ekstrand, B 18, 1207, J pr [2] 42, 375) Obtained also by saponifying its nitrile (Graeff, B 16, 2252) Needles, m sol hot alco hol —KA' aq —NaA' 2aq —CaA' 2 Baq 15° -BaA', 4aq

Methyl ether MeA' [112°] Needles Ethyl ether EtA' [109°] Needles Ethylether EtA' [109°] Isopropylether PrA' [76 Nitrile C₁₀H₆(NO₂)CN [1' [760] Needles [173°] by nitration of (β) naphthoic nitrile Needles

 (γ) Nitro- (β) naphthoic acid [269°] Formed

as above Needles, v sol alcohol

Ethy ether EtA' [93°] (δ) Ni ro-(β)-naphthoic acid

 $_{0}\dot{\mathbf{H}}_{0}(\mathrm{NO}_{2})(\mathrm{CO}_{2}\dot{\mathbf{H}})[4'\mathrm{or}1'2]$ [288°] S (alcohol) 25 in the cold Formed as above (Ekstrand, J pr [2] 42, 292) Needles Yields dinitro naphthoic acid [226°] with fuming HNO, -NH, A' -NaA' 2aq -BaA', 8aq -CaA', 41aq 8 15 in the cold

(ε)-Nitro (β) naphthoic soid [285° the products of the [285°] One of the products of the action of HNO, (S G 1 42) on (3) naphthoic acid (Ekstrand, J pr [2] 42, 304) Stellate needles (from alcohol)

Ethylether EtA' [75°] Needles

Di-nitro-(a) naphthoic acid $C_{10}H_5(NO_2) \stackrel{?}{\downarrow}CO_2H \stackrel{?}{\downarrow}4 \stackrel{4'}{\downarrow}1$ [265°] Obtained by nitration of (a) naphthoic acid and of (1,4')nitro naphthoic acid (Ekstrand, B 17, 1600, 19, 1984, 20, 219, 1353, *J pr* [2], 38, 259) Prisms or needles (from alcohol) Reduced by Reduced by tin and HClAq to naphthylene diamine [65° H S in alkaline solution forms $C_{10}H_5N_2CO_2H$ (?), a blush violet pp — NaA' 6aq — BaA', 21aq - CaA', 3aq needles S 7 in the cold Ethyl ether EtA' [143°] Needles

Di-nitro (a) naphthoic acid

C₁₀H (NO₂),CO₂H [215°] Formed, together with the preceding acid, by nitrating (a) naph thoic acid (Ekstrand, B 19, 1984, J pi [2] 38, 270) Needles or plates (from alcohol) Yields nitro amido naphthoic acid [c 110°] on reduc tion by H S and NH₃—CaA Ethylether EtA' [13

[1379] Needles

Di nitro-(α)-naphthoic acid

C₁₀H₁(NO)₂CO₂H [4'1'1] [218°] Formed by nitrating nitro (a) naphthoic acid [239°], and occurs among the products of the action of furning HNO3 on (a) naphthoic acid (Ekstrand, B 20, 220, J pr [2] 38, 267) Trimetric crystals (from alcohol), a b c - 973 1 1 442 Yields a lactum of di amido naphthoic acid on reduction -CaA', 7aq yellow needles, v e sol water

Ethylether EtA' [129°] Needles

Di nitro-(8) naphthoic acid

C₁₀H₅(NO₂) CO₂H [226°] S (alcohol) 17 in the cold Formed, together with the isomeride [148°] by dissolving (B) naphthoic acid in fuming HNO, Formed also, in like manner, from nitro (B) naphthoic acid [288°] (Ekstrand, B 17, 1602, J pr [2] 42, 300) Needles (from alcohol) Yields by reduction nitro amido naph Needles (from thoic acid [235°] and di amido naphthoic acid [c 230°] — NH₄A' aq S 35 in the cold —BaA', 6aq —CaA', 4aq S 06 in the cold

Ethylether EtA' Needles [141°]

Di-nitro-(B)-naphthoic acid

 $C_{10}H_{1}(NO_{2})_{2}CO_{2}H[\bar{1}\ 1'\ 2] \text{ or } [4\ 4'\ 2]$ [248°] (alcohol) 16 in the cold Formed as above, and also by nitrating nitro (\$\beta\$) naphthoic acid [293°] (Ekstrand, B 17, 1602, J pr [2] 42, 286) Rectangular prisms Reduced by FeSO, and NH₃ to di amido naphthoic acid [202°] -NHA' aq NaA' 4aq —BaA', 8aq —CaA', 5aq Ethyl ether EtA' [165°]

Tri nitro-(a) naphthoic acid C₁₀H₁(NO₂)₈CO₂H [283°] Formed in small quantity by the action of H₂SO₄ and HNO₂ on nitro (a) naphthoic acid [215°] (Ekstrand, B 19, 1131, J pr [2] 38, 372) Wedge shaped needles (from alcohol) Tastes very bitter -CaA'25aq

Ethylether EtA' [131°]. Prisms.

Tri nitro (a) naphthoic acid

C₁₀H₄(NO₂)₃CO₂H [236°] Formed from dinitro (a) naphthoic acid [265°], H₂SO₄, and fuming HNO₃ (Ekstrand, B 19, 1987) Needles Needles

Ethylether EtA' [191°] Tri-nitro (a) naphthoic acid

C₁₀H₄(NO₂)₂CO₂H [293°] A product of nitra tion of di nitro (a) naphthoic acid [265°] (E) Cubes, sl sol alcohol

Ethyl ether EtA' [150°] Needles

NITRO (a) NAPHTHOL

 $C_{10}H_6(NO_2)(OH)$ [2 1] [128°] Formed, together with the isomeride [164°], from acetyl- or benzoyl naphthylamine by nitrating and boiling the product with NaOHAq (Andreoni a Bieder mann, B 6, 342, Liebermann a Dittler, A 183, 245, Worms, B 15, 1815, Lellmann, B 19, Obtained also by oxidising (8) naphtho quinone (β) oxim (Fuchs, B 8, 629), and by the action of nitrous acid on (a) naphthylamine at 100° (Deninger, J pr [2] 40, 300) Yellow needles, sl sol water, m sol alcohol, volatile with steam —KA' aq —BaA', 3aq red needles
Nitro-(α) naphthol C₁₀H, (NO)(OH) [4 1]

[164°] Formed as above, and also by the ac tion of (nascent) nitrous acid on (a) naphthyl amine in the cold (Deninger, J pr [2] 40, 300) Golden needles (from water), not volatile with steam, v e sol alcohol Yields di nitio naph seeam, γ e soi arconor friends in flato hapit thol [138°] on nitration By successive reduction and oxidation it may be converted into (α) naphthoquinone – KA' – NaA'. 2aq crimson needles, bluish red when anhydrous – BaA 2 aq -BaA', 3aq (Hubner, A 208, 325) -CaA', 3aq -PbA', scarlet powder -AgA'

Nitro-(B) naphthol Ethyl ether [73°j $C_{10}H_{\bullet}(NO_{\bullet})(OEt)[1\ 2']$ Formed, to gether with the ethyl ethers of the two following isomerides, by nitrating C₁₀H (OEt) dissolved in HOAc (Gaess, J pr [2] 43, 25) Needles

Nitro-(B) naphthol Ethylether $C_{10}H_{\scriptscriptstyle 0}(NO_2)(OEt)$ [2 2'] [114°] Needles Yields on oxidation nitrophthalic acid [114°]

 $Nitro-(\beta)$ -naphthol $C_{10}H_6(NO_2)(OH)[1\ 2]$ [103°] Formed by oxidising the (a) oxim of (B) naphthoguinone (Stenhouse a Groves, C J32, 51), or by boiling the acetyl derivative of nitio (3) naphthylamine with NaOHAq (Lieber mann'a Jacobson, A 211, 46) Formed also by the action of (nascent) nitrous acid on (3) naph thylamine (D) Needles By reduction fol lowed by oxidation it may be converted into (8) naphthogumone

Acetylderivative C10H6(NO2)(OAc) [61°] Yields C₁₀H_s(NHAc)(OH) on reduction by zinc dust and HOAc (Bottcher, B 16, 1933)

Bensoyl derivative C10Ho(NO2)(OBz) [142] Yields $C_{10}H_0(NHBz)(OH)$ on reduction Ethyl ether Eth' [104°] Yellow needles (Wittkamp, B 17, 393, Gaess, J pr [2] 48, 22)

Di nitro (a) naphthol C10H5(NO2)2(OH)[4 2 1] Martrus yellow [1380] Formed by the action of HNO, on (a) naphthol, (a) naphthol sulphonic acid, and (2,1)- or (4,1)-nitro naphthol (Martius, Z [2] 4,80, Darmstadter a Wichelhaus, A 152,299, Liebermann, A 183, Formed also by boiling diazonaphthalene 249) chloride or sulphonate with dilute nitric acid (Martius, Nevile a Winther, C J 37, 632) Sulphur yellow crystals, nearly insol boiling water, al sol alcohol. Not volatile with steam. Yields phthalic acid on oxidation Its salts dye wool yellow Poisonous 4 g killed a dog (Weyl, B 21, 2191) — NH, A' aq — Na, A'' aq — CaA', 6aq — SrA', 3aq — BaA', 3aq — AgA' Ethyl ether EtA' [88°] Needles

Dı nitro (β)-naphthol

C₁₆H₅(NO₂)₂(OH)[1 2' 2] [194°] Formed by heating (β) naphthol with alcohol and HNO₂ Formed by (Wallach a Wichelhaus, B 3, 846) Prepared by boiling a solution of (B) diazonaphthalene chloride with HNO₃ (Graebe a Drews, B 17, 1170) Yellow needles Dyes deep yellow On oxidation it yields nitro phthalic acid [160°] KA'2aq yellow needles —Ba'A, aq (Löwe, B 23, 2542) — AgA' scarlet pp Ethylether EtA' [138°] (Graebe), [144°]

(Gaess) Formed by nitrating the compounds $C_{10}H_g(NO_2)(OEt)$ [114°] and [104°] needles Converted by NH, into di nitro naph

thylamine [238°]

Di nitro-(B) naphthol

 $C_{10}H_5(NO_2)_2(OH)[11'2']$ [198°] Formed from its ether by saponifying with alcoholic potash Plates Yields nitrophthalic acid [212° or 218°] on oxidation

[215°] Obtained by Ethyl ether EtA' [215°] Obtained by nitrating C₁₀H₆(NO₂)(OEt) [1 2] (Gaess), and also from the [12] isomeride Needles Possibly identical with the following isomeride

Di nitro-(β) naphthol

nitro phthalic acid on oxidation

Tri nitro-(a) naphthol $C_{10}H_4(NO_2)_8(OH)$ [176°] S 28 at 15° Formed from di nitro (a) naphthol, H₂SO₄, and HNO₃ (Ekstrand, B 11, 161, Diehl a Merz, B 11, 1662) Small crystals Yields di nitro phthalic acid [213°] on oxidation—KA' aq S 25 m the cold— S 3 in the cold -NH₄A' S 15 in NaA' aq the cold —BaA', 2 aq S 09 —CaA', 3 aq S 4 -AgA

[128°] Methyl ether MeA' nitrating C, H,OMe (Staedel, B 14, 899, A 217, Yellow plates

Ethyl ether EtA' [148°]

Tri nitro- (β) naphthol $C_{10}H_4(NO_2)_8OH$ Methyl ether MeA' [213°] Ge [213°] Got by nitrating C₁₀H₇OMe (Staedel)

Ethyl ether EtA' [186°]

Tetra-nitro-(a)-naphtholC₁₀H₂(NO₂),OH [180°] S (benzene) 45 at 18° Formed by boiling C₁₀H₃Br(NO₂)₄ [170 5°] with Na₂CO₃Aq (Merz a Weith, B 15, 2714) Yields di nitrophthalic acid [227°] on oxidation -NaA' 2aq S 1 at 19° — CaA', 2aq — BaA', 3aq — AgA' 3aq red needles

SULPHONIC DI-NITRO-(a)-NAPHTHOL ACID C1.H.N.SO. 10

 $C_sH_s(SO_sH) < C(OH) C(NO_s) CH$ Naphthol yellow

S Formed by warming (a)-naphthol trisulphonic acid with adduct nitric acid at 50° (Lauter bach, B 14, 2028) Obtained also from monoor di sulphonic acids of (a)-naphthol in which one SO.H is in a different ring to the hydroxyl. Long yellow needles. Very powerful dye, producing a very fast greenish-yellow shade ---

K₂A" v si sol cold water Not poisonous (Weyl, B 21, 2191)

Di nitro-(α)-naphthol sulphonic acid

 $C_{10}H_4(NO_2)_2(OH)(\overline{SO_3H})[4' \times \overline{2} \ 4]$ Crocem yellow Formed by warming (β) naphthol (a) sulphonic acid with dilute HNO_8 (Nietzki a Zübelen, B22, 454) -KA' golden scales

NITRO-(\$)-NAPHTHOQUINONE

 $C_{10}H_3(NO_2)O_2$ [158°] Formed by nitrating (8) naphthoquinone (Stenhouse a Groves, A 194, 203, C J 33, 416, 45, 299) Crimson plates (from HOAc), sl sol ether and water With alcoholic aniline it forms the compound $C_{10}H_4(NO_2)(OH) < {}^{O}_{NPh} [253^{\circ}] (Korn, B 17, 908)$ p Bromo aniline forms the corresponding body $C_{10}H_4(NO_2)(OH) < V_{N C_2H_4Br}$ [245°] (Brauns, B The corresponding o toluide melts at 240°, the p toluide at 241° Excess of aniline in benzene forms yellow needles of C16H14N2O4 Hydroxylamine hydrochloride in pre sence of HOAc forms a salt C10H3NO4(NH2OH) [141°], which on boiling with HOAc yields nitro hydro- (β) naphthoquinone (Zaertling, B 23, 179)

Nitro-(γ) naphthoquinone [208°] Formed by oxidising nitro acenaphthene (Quincke, B 21, Yellowish red needles vielding with aniline C₁₀H₄O₂(NO₂)(NHPh) [128°], and, with diphenylamine, $C_{10}H_4O_2(NO_2)(NPh_2)$

NITRO-(αα)-DINAPHTHYL C₁₀H, C₁₀H₆NO, [188°] Formed from dinaphthyl, HNO₃, and HOAc (Julius, B 19, 2549) Orange plates

Di-nitro-dinaphthyl C₁₀H₆(NO₂) C₁₀H₆(NO₂) [280°] Formed by intrating disaphthyl (J) Yellow needles, insol alcohol, v sl sol $C_{\rm g}H_{\rm g}$

Tetra-nitro-dinaphthyl C₂₀H₁₀(NO₂), Formed from dinaphthyl and fuming HNO₃ (Lossen, A

 144, 77) Amorphous orange powder
 Tetra-natro-(ββ) dinaphthyl [150°] Formed from isodinaphthyl and HNO, (Staub a Watson Smith, C J 47, 104) Amorphous yellow powder

NITRO-(a)-NAPHTHYL-AMIDO-BENZOIC **ACID** $C_{10}H_7NH$ $C_6H_8(NO_2)$ $CO_2H[131]$ Formed by heating (a) naphthylamine with bromo nitro benzoic acid (Heidenleben, B 23, 3158) Yields on reduction the amido- acid [90°] -NaA dish brown powder

Ethyl ether EtA' [109°]

Nitro (β) - naphthyl - amido - benzoic Formed in like manner from (B) naphthylamine) Brick-red crystals, msol water —NaA' Ethyl ether EtA' [127 5°]

NITRO (a) NAPHTHYLAMINE

C₁₀H_s(NO₂)(NH₂)[2 1] [144°] Formed by saponifying its acetyl derivative, which is pro Formed by saduced, together with that of the (4, 1) isomeride [190°], by nitrating the acetyl derivative of (a)-naphthylamine (Lellmann a Remy, B 17, 109, 19, 236, 796) Red monoclinic prisms (from alcohol) Converted by boiling alcoholic potash into nitro-naphthol [128°]

Acetyl derivative C₁₀H₆(NO₂)(NHAc) [199°] With 1 mol of the (4, 1)-isomeride it

forms a compound [170°]

Dr-acetyl derivative C10H6(NO2)(NAc2) [115°] Got by using Ac₂O at 140°

Bensoyl derivative C₁₀H₅(NO₂)(NHB₂) [175°] (Worms, B 15, 1814) Yields benzenyl-

naphthylane diamine [210°] on reduction with tin and HCl (Hubner, A 208, 324)

Nitro (a)-naphthylamine

 $C_{10}H_{\circ}(NO_2)(NH_2)[4\ 1]$ [190°] Formed as above (Liebermann, A 183, 232, L a R) Orange needles (from alcohol) Yields naphthylenediamine [186°] on reduction

Acetyl derivative [144°]
Dr acetyl derivative [144°]
Yields nitronaphthol [164°] on boiling with potash

Nitro (a) naphthylamine

 $C_{10}H_6(NO_2)(NH_2)[4'1]$ [119°] Formed by re duction of 'a' di nitro naphthalene with alco holic NH₃ and H₂S (Beilstein a Kuhlberg, A 169, 81) Small red needles (from water) Or elimination of NH2 it yields (a) nitro naphthal ene -B'2H2SO 2aq needles, sl sol cold water

Sulphonic acid $C_{10}H_{5}(NO_{2})(NH_{2})(SO_{3}H)[4'14]$ Formed from (1, 4) naphthylamine sulphonic acid by acetyla tion, nitration, and subsequent saponification (Nietzki a Zubelen, B 22, 451) Colourless needles Potash yields nitro naphthylamine

Nitro (β) naphthylamine $C_{10}H_c(NO_2)(NH_2)[1\ 2]$ [127°] (L a J), [124°] (Meldola, C J 47, 520) Formed by saponifying its acetyl derivative, which is obtained by nitra ting the acetyl derivative of (β) naphthylamine (Liebermann a Jacobson, B 14, 806, 1792, A211, 42) Orange needles, sol hot water

Acetyl derivative C₁₀H₄(NO₂)(NHAc) [124°] Reduced by tin and HOAc to ethenyl $(\alpha \beta)$ naphthylene diamine (Fischer a Hepp, B

20, 2473)

Di nitro (a)-naphthylamine $C_{10}H_{4}(NO_{2})_{2}(NH)$ [4 2 1] [239°] (Witt, B 19, 2032) Obtained from its acetyl derivative, which is formed by nitrating C10H NHAc The suponification is effected by alcoholic NH_s or by \hat{H} SO₄ (Liebermann, A 183, 274, Meldola, B 19, 2683) Formed also by heating di nitro (a) naphthol with alcoholic NH, Readily con Lemon yellow needles verted by potash into di nitro a naphthol elimination of NH, it yields di nitro naphthal ene [144°]

Acetyl derivative [250 5°] (Ebell, A 208,

330), [247°] (L) Needles

Benzoyl derivative [252°] Needles Di nitro-(8) naphthylamine

 $C_{10}H$ (NO $)_2(NH_2)$ [242°] Formed by heating $C_{10}H_2(NO_2)_2(OEt)$ [144°] with aqueous NH_3 at 140° (Graebe a Drews, B 17, 1172, Gaess, J pr [2] 43,31) On elimination of NH₂ it yields di nitro naphthalene [1615°] or [167°] Two iso meric compounds C10Ha(NO2)2NHAc [185°] and [235°] are got by nitrating acetyl (8) naphthylamine (Maschke, C C 1886, 824)

Di-nitro (8) naphthylamine $C_{10}H_1(NO_1)_2(NH_2)$ [1 1' 2'] [228°] from $C_{10}H_3(NO_2)_2(OEt)$ [215°] (Gaess) di nitro naphthalene [172°] Formed Yields

Di-nitro-naphthylamine obtained from the C₁₀H₅(NO₂)₂(OEt) [215°] of Onufrovitch (B 23, 3562) carbonises at 235°-250°

Tri-nitro-(a)-naphthylamine

 $C_{10}H_4(NO_2)_8(NH_2)$ [c 264°] Formed from Closed (No. 1), OEt and alcohole NH, at 50° (Staedel, B 14, 901, A 217, 173) Yellow prisms (from toluene) On elimination of NH; it yields tri nitro naphthalene [181°]

Tri-nitro (β) naphthylamine. Formed from $H_4(NO_2)_3$ Oht and NH_2 (S) Yellow needles C₁₀H₄(NO₂)₃ Oht and NH₃ (S) Yields tri nitro-naphthalene [181°] on elimina tion of NH2

Tetra nitro-(a)-naphthylamine C10H3(NO2)1NH2. [194°] Formed from $C_{10}H_3Br(NO_2)_4$ and NH_3 (Merz a Weith, B 15, 2718) Yellow needles, sl sol alcohol

Tetra-nitro-(β) naphthylamine [202°] Formed from (B) bromo tetra nitro naphthalene and NH, (M a W) Yellow needles

Nitro-di-(B)-naphthyl amine Benzoyl de rivative $C_{10}H_7$ NBz $C_{10}H_6$ NO₂ [168°] nitrating $(C_{10}H_7)_2$ NBz (Ris, B 20, 2625) Got by Nodules (from alcohol) or prisms (containing C_sH_s) [95°] (from benzene) Yields, on reduction, benzenyl naphthylene naphthyl-diamine [163°]

Di nitro di (β) -naphthyl-amine

 $C_{20}H_{12}(NO_2)_2NH$ [225°] Formed from di (\$\beta\$) naphthyl amine, HOAc, and HNO, (Ris a. Weber, B 17, 197)

Tetra nitro-di-(β)-naphthyl amine $C_{20}H_{10}(NO_2)_4NH$ [286°] Formed by mixing di (8) naphthylamine, HOAc, and HNO, without cooling (R a W) Granules On further nitra tion it yields hexa-nitro di naphthyl amine

NIŤRO NAPHTHYLENE DIAMINE acetyldericative C10H3(NO)(NHAc) [241] [c 295°] Formed by nitrating C₁₀H₆(NHAc) (Kleemann, B 19, 335) Yellow needles, yield ing phthalic acid on oxidation

DINITRO-(α) DINAPHTHYLENE-OXIDE $\mathbf{C}_{20}\mathbf{H}_{10}(\mathrm{NO}_{2})\mathbf{O}$ [270°] Prepared by nitration of

(a) dinaphthylene oxide (Knecht a Unzeitig, B 13, 1725) Yellow needles

Dinitro (3) dinaphthylene-oxide

C ₀H₁₀(NO₂)₂O [221°] Prepared by nitration of (B) dinaphthylene oxide (K a U) Orangered needles

TETRA NITRO DI NAPHTHYL METHANE $CH_{2}\{C_{10}H_{5}(NO_{5})_{2}\}_{2}$ Formed from naphthyl methane and HNO3 (Grabowski, B 7, 1605) Colourless crystals, decomposing at 260°-

NITRO-(a) NAPHTHYL PIPERIDINE

[**77°**] $\mathbf{C}_{10}\mathbf{H}_{6}(\mathbf{NO}_{2})\dot{\mathbf{N}}\dot{\mathbf{C}}_{5}\mathbf{H}_{10}$ Formed by heating (1, 4) bromo nitro naphthalene with piperidine (Lellmann a Buttner, B 23, 1387) Yellow needles Weak base

DI NITRO DI-(a) NAPHTHYL DISULPHIDE Formed from nitro $S(C_{10}H_6NO_2)_2$ [186°] naphthalene sulphonic chloride and HI (Cleve, B 23, 960) Greenish yellow scales

NITRO-NITROSO-ANTHRONE C, H, N O [263°] Formed by boiling hydroanthracene nitrite (vol 1 p 277) with alkalis (Liebermann a Landshoff, B 14, 470) Yellow needles, yielding anthraquinone on oxidation

NITRO-OCTANE C.H.NO. (205°-212°)
Formed by distilling octyl rodide with AgNO. (Eichler, B 12, 1883)

NITRO-OCTOIC ACID C₈H₁₈(NO₂)O₂ 18 1093 Formed by boiling the non volatile acids of cocoa nut oil for a long time with HNO, (Wirz, A 104, 289) Oil — AgA' — EtA' S G 18 (W1rz, A 104, 289) 1 031

NITRO-OCTYL-BENZENE C.N. (NO2)C.H., The three isomerides may be got by nitrating octyl benzene (Ahrens, B 19, 2721) o Nitro octyl benzene carbonises at 130°, the m iso meride melts at 124°, the p-variety melts at

They yield the corresponding nitro benz one acids on oxidation by KMnO

C,H,(NO,),C,H,, Di-nitro-octyl-benzene [226°] Formed by nitration of octyl benzene NITRO-OPIANIC ACID v OPIANIC ACID

NITRO ORCIN C,H,NO, 1 e

 $C_aH_2Me(NO_2)(OH)_2$ Two nitro orcins [120°] and [115°] are formed, together with an azo compound, by the action of a cold mixture of nitrous and nitric acids on an ethereal solution of orcin (Weselsky, B 7, 439) They may be separated by steam distillation, the compound melting at 120° being volatile. The nitro orein [120°] forms Ba(HA")₂, the isomeride [115°] yields Ba(HA")₂8aq and BaA" 3aq. By the action of HNO₃ and HNO₅ on the ethyl derivative of orcin there are formed two compounds $C_6H_2Me(NO_2)(OH)(OEt)$, melting at 54° and 103° respectively (Weselsky a Benedikt, M 2,

Di-nitro-oroin C₆HMe(NO₂)₂(OH)₂ [164 5°] S (alcohol) 55 at 15° Formed from di nitroso-orcin and cold dilute HNO, (S G 13) (Sten house a Groves, A 188, 358) Yellow plates, m sol boiling water May be sublimed—

Ba(HA"), aq

Di-nitro-orcin [110°] Obtained by satu rating toluene with NO₂ (Leeds, A C J 2, 416, B 14, 483) Golden needles (from alcohol)

Dyes silk yellow

Tri-nitro-orcin C₆Me(NO₂)₃(OH) Formed from orcin, H2SO4, and HNO3 (Sten house, Pr 19, 410, Merz a Zetter, B 12, 681) Yellow needles, v sol hot water Exploder above 163° Dyes the skin yellow $-K_2A''$ orange needles -BaA'' 3aq -PbA'' $-Ag_2A''$ Explodes amorphous orange red pp

Methyl ether Me,A" [69 **5**]. Ethyl ether Et2A' [615°

NITRO-OXINDOL C₈H₈ON(NO₂) Prepared by adding powdered KNO₂ to a solution of oxindol in H₂SO₄ (Baeyer, B 12, 1313) Yellow needles, sol alcohol Begins to decompose at 175°

p NITRO ω OXY-ACETOPHENONE $C_0H_4(NO_2)$ CO CH_2OH [121°] Fo Formed by boiling bromo nitro acetophenone with NaOAc and HOAc, diluting with water, and boiling again (Engler a Zulke, B 22, 204) Sol hot alkalıs

Nitro-di-oxy-acetophenone

C_sH₂(NO₂)(OH)₂ CO CH₃ [142°] Formed nitration (Nencki a Sieber, *J pr* [2] 23, 537) Formed by

TETRA NITRO OXY AMIDO ANTHRAQUI-NONE C₁₄H₂N₅O₁₁ te C₁₄H₂(NO₂)₄(NH₂)(OH)O₂ Chrysammidic acid Formed by boiling chrys ammic acid C₁₄H₂(NO₂)₄(OH)₂O₂ with ammonia (Schunck, A 65, 236, Graebe a Liebermann, A Suppl 7, 310) Olive green needles, forming a dark purple aqueous solution Its salts explode when heated

NITRO OXY AMIDO BENZOIC ACID

 $C_1H_6N_2O_5i e C_6H_2(NO_2)(OH)(NH_2)CO_2H[5 2 3 1]$ Got by reducing di nitro o oxy benzoic acid (Hubner a Babcock, B 12, 1345) Crystals

NITRO-OXY-AMIDO DIPHENYL Acetyl derivative C₆H₄(NHAc) C₆H₃(NO₂)(OH) [264°] (Schmidt a Schultz, A 207, 347) Yellow needles

NITRO-DI-OXY-DI AMIDO TRI PHENYL METHANE Di methyl-ether

C_eH₄(NO₂)CH(C_eH₃(OMe)NH₂)₂ [108°] Formed by heating p ratro benzoic aldehyde with anis-

idine sulphate and H_2SO_4 (Fischer, \sharp 15, 680) Golden needles (containing C_6H_6) \sharp Anisidine yields an isomeric body [189°] (Kock, B 20, 1562)

NITRO DI OXY AMIDO QUINONE C, H, N, O, te C₆(NO₂)(OH)₂(NH₂)O₂ The salt C₆H₂K₂N₁O₆

15 precipitated on exposing a solution of C₆(NO₂)(NH₂)(OH)₄ in aqueous K₂CO₃ to the art (Nietzki a Benckiser, B 18, 499) coppery needles

NIŤRO OXY ANTHRAQUINONE Ethyl $C_6H_4 < CO > C_6H_2(NO_2)(OEt)$ [243°] Formed by oxidation of the nitroso

anthrone of the ethyl ether of nitro anthrol (Liebermann a Hagen, B 15, 1795) needles, sl sol alcohol Colourless

Nitro-di-oxy-anthraquinone C14H,(NO2)O4 (a) Nitro alizarin [196°] Prepared by nitra tion of the diacetyl derivative of alizarin (Schunck a Romer, B 12, 587) Less soluble in alcohol and HOAc than the (B) isomeride Oxidised by HNO, to phthalic acid Yields

purpurin on warming with H SO.

Nitro-di-oxy-anthraquinone (β) Nitro alizarın Alızarın orange [244°] Formed by nitration of alızarın dissolved in HOAc (S a R, Rosenstiehl, Bl [2] 26, 63) Formed also by boiling di nitro oxy anthraquinone with dilute (20 pc) NaOH (Simon, B 15, 692) Orange needles (from benzene), sl sol KOHAq Dyes alumina mordants red and iron mordants reddishviolet

Di-acetyl derivative [218°] Needles Nitro-tri-oxy-anthraquinone C_{1,}H₇(NO)O₅ Formed from alizarin and fuming HNO₂ (Strecker, Z 1868, 264) Red crystalline pow der —K₂A"

Di-nitro-oxy-anthraquinone

 $C_6H_4C_2O_2C_6H(NO_2)_2(OH)[1 3 2]$ [270°] Formed from oxy anthraquinone and fuming HNO₃ (Simon, B 14, 464, 15, 694) Yellow needles Dyes wool and silk orange —KA'— CuA'₂2aq —MgA'₂5aq —AgA' Ethyl ether EtA' [158°]

Di nitro di oxy anthraquinone

C₁₄H₆(NO₂)₂O₄ Di nitro-purpuroxanthin [250°] Formed from purpuroxanthin and cold HNO, (S G 148) (Plath, B 9, 1205) (from HOAc) — NH₄HA" — BaA" Red needles red needles

Tetra-nitro di oxy anthraquinone C14H4(NO2)4O4 Tetra netro anthraflavic acid Tetra nitro anthraflavone Formed by boiling anthraflavic acid with HNO₃ (S G 14) (Schard inger, B 8, 1487) Yellow needles, melting with explosion at 307 6° cor—Salts—(NH₄)₂A"— $(NH_4)_2A''NH_3 - (NH_4)_2A''2NH_3 - Ag_2A''$ ish needles

Tetra-nitro-di-oxy-anthraquinone

C₁,H₄(NO₂),O₄ Tetra-mirro isoanthrafiavic acid. Formed by nitrating isoanthrafiavic acid (Roemer a Schwarzer, B 15, 1045) Yellow plates (from dilute HNO₄). Its alkaline solution is red Dyes wool and silk orange yellow, but does not combine with mordants - K,A"2aq silky red needles

Tetra nitro-di-oxy-anthraquinone C14H4(NO2)4O. Tetra netro anthrarufin Formed by nitration of anthrarufin (Liebermann, B 12, 188) Small yellow plates (from fuming HNO₃) -Na₂A'' 4aq — K₂A'' aq: bronze coloured prisms. MgA" 6aq

Tetra-nitro di-oxy-anthraquinone

C₁₄H₄(NO₂)O₄ Chrysammic acid Formed by heating aloes with HNO, (S G 137) (Schunck, 4 39, 1, 65, 235, Stenhouse a Muller, C J 19, 319, Tilden, Ph [3] 2, 845) Formed also by nitration of chrysazin (di oxy anthraquinone) (Liebermann a Giesel, B 8, 1643, 9, 329, A183, 193) Golden plates or monoclinic prisms Explodes when quickly heated Aqueous potas sium cyanide at 60° forms chrysocyammic

acıd C₁₈H₈N₈O₁₂ 6aq, which forms the dark red salts (NH₁).A' 3aq, K₂A'' 3aq, and CaA'' 3aq
Salts —Na,A'' 3aq (Mulder, A 68, 339, 72,
285)—K₂A'' S 08 in the cold Flat rhom boidal plates, polarises light, the two rays being differently coloured (Brewster, P 69, 552, Hirschwald, A 183, 198) — BaA" 2aq — BaA" 4aq — MgA" 5aq — PbA" 5aq — PbA" (OH)₂ —

PbA" 4aq —MnA" 5aq —CuA" 4aq Ethyl ether Et,A" Pale re Pale red needles or yellow prisms (Stenhouse)

Benzoylderivative C₁₄H₂Bz N₄O₁₂

Yellow, almost insoluble, prisms

NITRO-OXY-BENZENE v NITRO PHI NOL Nitro tri oxy benzene Tri methyl deri $vative C_0H_2(NO_2)(OMe)_3 [x 1 2 3]$ [100] Formed from C, H₃(OMe)₃ and conc HNO₃ (Will, B 21, 612) Thick prisms With HNO₃ it yields C,H(NO₂)₂(OMe)₃ [126°], al sol alcohol

Di-nitro tetra-oxy-benzene Methylene di methyl derivative Di nitro apione C₆(NO)₂(OMe)₂<0>CH [118°] Formed from apiolic acid (4 g), HOAc (50 cc), and HNO (100 cc of S G 1 4) (Ciamician a Silber, B 22, 2489, 23, 2290) Yellow needles, insol water Yields on reduction C₈H₈O₄(NH)₂ [119°] diacetyl it condenses to $C_{13}H_{11}N_2O_4$ [176°], and with benzil to $C_9H_8O_4{\stackrel{\frown}{N}}{\stackrel{\frown}{N}}{\stackrel{\frown}{CPh}}$ [222°], both crys

tallising in needles

NITRO-o-OXY-BENZOIC ACID

 $C_6H_3(NO_2)(OH)(CO_2H)[5\ 2\ 1]$ Nitro salicylic acid Anilotic acid [228°] Mol w 183 S 176 at 22° (Hubner), 07 at 155° (Schiff) Formed, together with the isomeride [144°], by the action of nitric acid on salicylic acid and on Indigo (Chevreul, A Ch [1] 72, 131, Buff, A Ch [2] 37, 160, Dumas, A Ch [2] 63, 205, [3] 2, 227, Gerhardt, A Ch [3] 7, 325, Marchand, J pr 26, 385, Piria, A 56, 35, Stenhouse, A 70, 253, Schiff, A 154, 14, Schiff a Masino, G 9, 318, A 198, 258, Hubner, A 195, Formed also by the action of aqueous NaNO, and H2SO, on salicylic acid at 50° (Deninger, J pr [2] 42, 550), by boiling (ϵ) nitro amido benzoic acid [263°] with potash (Griess, B 11, 1730), and by heating p nitro phenol with COl. and alcoholic potash at 1005 (Hasse, B 10, 2188) White needles, v sol alcohol Its aque Distillaous solution is coloured red by FeCl, tion with CaO yields p nitro phenol [114°]

Salts - KA' - NH, A' - BaA', baq -BaC,H,NO, 2aq — CaA', 6aq — SrA', 5\frac{1}{2}aq — MgA', 4aq — ZnA', 5aq — AgA'

Methylether MeA' [88°] Formed from methyl salicylate and nitrous acid (Deninger, J pr [2] 40, 302)

Ethyl ether EtA' [94°] Needles. Methyl dersvatsve C₂H₂(NO₂)(OMe)(OO₂H) [149°] Formed from

C₆H₄(OMe)(CO₂H) and HNO₂ (Kraut, A 150, 6, Salkowski, A 173, 41) Needles Gives no colour with FeCl3

Ethyl derivative C₆H₃(NO₃)(OEt) CO₂H [163°] (P), [161°] (K) Formed from ethoxy benzoic aldehyde C₆H₄(OEt)CHO and conc HNO₂ (Perkin, A 145, 311) Formed also from $C_6H_4(NO_2)(OH)$ CO₂Me, EtI, and KOH, the resulting $C_6H_4(NO_2)(OEt)$ CO₂Me being saponified (Kraut) Plates from boiling water) —BaA'₂2aq [98°] (Hubner)

Amide C,H,(NO2)(OH) CONH2 Behaves as an acid, decomposing Needles carbonates, and forming the salts C H KN O, aq

-CaA'₂ 4aq —BaA', 4aq —PbA', 4aq Anilide C₂H₃(NO₂)(OH) CO NHPh [224°] Formed by nitrating C₆H₄(OH) CONHPh (Men

sching, A 210, 343) Needles

Nitro-o-oxy-benzoic acid $C_bH_s(NO)(OH)CO_2H[321]$ [144°] S 13 at (Schiff) Formed as above, and also by adding H.SO, to a solution of salicylic acid and NaNO, at 100° (Deninger, J pr [2] 42, 551), and by the action of nitrous acid on oil of wintergreen (Smith a Kneil, Am 8, 100) tained also by heating o nitro phenol with CCl. and alcoholic potash at 100' (Hasse) Needles (containing aq) Melts at 125° when hydrated, 144° when annydrous FeCl_s colours its solution red Yields o nitro phenol on heating with dılute H₂SO, at 150°

Salts - NaA' - KA' - BaA'2. Needles -BaC H₃NO₅ 1½aq — MgA' 2aq — PbC H₃NO₅ — AgA

Ethyl ether EtA' [118°]

Amide C,H,(NO)(OH) CONH2 [146°] Needles Yields the salts Ca(C, H, N, O,) 4aq -BaA', 2aq -Pb(OH)A' 2aq

Nitro o-oxy benzoic acid C, H, NO, i e C₆H₃(NO₂)(OH)(CO₂H)₁621] A mide of the methyl derivative C,H,(NO)(OMe)CONH [195°] Formed by boiling its nitrile with baryta water (Lobry de Bruvn, R T C 2, 217)

lowish needles, m sol acetone

Nitrile of the methyl derivative

C_bH₃(NO)(OMe)CN [171°] Formed by boiling m di nitro benzene with KCy and MeOH (Lobry de Bruyn, R T C 2, 212) Nicelles (from alco Boiling alcoholic potash converts it into hol) C₆H₃(OH)₂CO₂H

of thederivative Amideethyl $C_6H_3(NO_2)(OEt) CONH_2 [197°]$ Needles

Nitrile of the ethyl derivative $C_8H_3(NO_2)(OEt)CN$ [137°] bound from m dinitro benzene and alcoholic KCy Tables

a Nitro m oxy benzoic acid

C₀H₃(NO₂)(OH)CO₂H[6 3 1] [169°] Formed by boiling (a) nitro amido benzoic acid with potash (Griess, B 11, 1733) Light yellow crystals containing aq), v sol water —BaC,H,NO, 6aq orange prisms

Methyl derivative [188°] $C_6H_1(NO_2)(OMe)(CO_2H)$ Formed by oxidising C.H.(NO₂)(OMe)CHO with KMnO₄ (Rieche, B 22, 2354)

β Nitro-m oxy benzoic acid C₆H₃(NO₂)(OH)CO₂H[4 3 1] [230°] Formed by boiling the corresponding nitro amido-benzoic acid with KOHAq and, together with the (2,3,1) and (5,3,1) isomerides, by nitration of a boiling aqueous solution of m oxy-benzoic acid by HNO, (Griess, B 5, 856, 20, 403). Yellow plates (from hot water) -BaC, H, NO, aq

Nutrile C.H. (NO2) (OH) CN [183°] From m oxy benzoic nitrile and HNO₃ (Smith, J pr [2] 16, 227) Coloured dark red by aqueous FeCl₃ Belongs perhaps to one of the isomeric nitro-m-oxy-benzoic acids

(γ)-Nitro-m-oxy-benzoic acid C_eH₂(NO₂)(OH)CO₂H[2 3 1] [178°] Formed by boiling (2,8,1)-nitro amido benzoic acid with potash, and also by nitrating m oxy benzoic acid (Griess, B 11, 1784, 20, 408) Yellow plates or Tastes sweet prisms (containing aq)

Bah', liaq

Methyl derivative C.H. (NO.) (OMe) CO.H.

[251°] Formed from its aldehyde and Ag.O. (Ricche, B 22, 2352) White plates —AgA'

(()-Nitro-m oxy-benzoic acid C_eH₂(NO₂)(OH)CO₂H[5 3 1] [1 C_sH₃(NO₂)(OH)CO₂H[5 3 1] [167°] Formed by nitrating m-oxy benzoic acid (v supra) Crystals (containing aq) —BaA'2 6aq

ystals (containing aq) —BaA', 6aq prisms

Methyldervative C.H.(NO.)(OMe)CO.H

3 Long white needles (Rieche, B 22, [233°] 2356)

δ-Nitro p-oxy-benzoic acid

C₆H₃(NO₂)(OH) CO₂H[3 4 1] [185°]

Formation -1 By dissolving p oxy-benzoic acid in dilute nitric acid (Barth, Z 1866, 647, Griess, B 20, 408) -2 By boiling (3,4,1)nitro-amido benzoic acid with potash (Griess, B 5, 856) -3 By the action of aqueous NaNO, and H₂SO₄ on p-oxy benzoic acid at 40° (Deninger, J pr [2] 42,552) -4 In small quantity in the action of CCl, and alcoholic potash on o nitro phenol (H)

Properties -Needles, sl sol hot water

Gives no colour with FeCl,

Salt -BaC, H, NO, aq red nodules Methyl derivative C₆H₃(NO₂)(OMe)CO₂H Nitranisic acid [187°] Formed by boiling anisic acid or oil of anise with nitric acid (Lau rent, B J 23, 416, Cahours, A 41, 71, Engelhardt, A 108, 243, Salkowski, A 163, 6, B 10, 1254) Also from C.H. (NO.) (OMe) CH. NHAc by oxidation with K. Cr. O. (Goldschmidt a Polonowska, B 20, 2410) Small needles (from water) Yields o-nitro phenol on heating with water at 220° - NaA'aq - KA'aq - CaA'₄ 4aq - SrA'₂ 4aq - BaA'₂ flocoulent pp - PbA'₂ - AgA' Methyl ether of the methyl derevative

 $C_eH_q(NO_2)(OMe)CO_2Me$ [108°] Plates

Ethyl ether of the methyl derivative

C.H.(NO₂)(OMe)CO₂Et [100°] Tables Nitrile of the methyl derivative C.H.(NO₂)(OMe) CN [150°] Formed from C.H. (OMe)CN and HNO, (Henry, B 2, 668) Small needles (from alcohol)

Natro di-oxy-benzoac acid Dr methylde Nitro di-oxy-benzolo solo Dr metnyl ac rvvatve C₆H₂(NO₂)(OMe)₂CO₂H[4 5 3 1] [225°] Formed from C₈H₂(OMe)₂CO₂H and dilute HNO₂ (H Meyer, M 8, 431) Needles (from water) Yields on reduction, C₆H₂(NH₂)(OMe)₂CO₂H [182°] — CuA'₂ 2½sq — PbA'₂ — AgA' needles Nitro-di-oxy-benzolo sold Methyl derra-

C_eH₂(NO₂)(OH)(OMe)CO₂H[x 4 3 1] te acid White needles (Matsmoto, Nitro-vanille acid

B 11, 122)

Acetyl derevative $C_eH_2(NO_2)(OAc)(OMe)CO_2H$ [182°] Needles Di-methyl derivative CH_(NO)(OMe),CO,H Nitro veratric

Yellow needles (containing | aq) | its methyl ether melts at 144° and its ethyl ether at 100°

Di-nitro-oxy-benzoic acid C_cH₂(NO_c)₂(OH)CO_cH[5 8 2 1] Dr netro-sale cylic acid [173°] Formed by nitration of salicylic acid (Cahours, A Ch [3] 25, 11, Sten house, A 78, 1, Hubner, A 195, 45) Tables or needles (containing aq) After fusion it melts at 158° FeCl. colours its solution red melts at 158° FeCl₂ colours its solution red — NH₄A'—KA' sl sol water — K₂C₂H₂N₂O₇ aq —BaC,H₂N₂O, 3aq m sol water -NaA' -BaA', needles -CaA' 22aq -PbC, H N2O, 3aq sparingly soluble granules

Methyl ether MeA' [127°] Yellowish scales Yields NH₂C₂H₂N₂O, and AgC₃H₁N₂O, Ethyl ether Eth [99°] Yields the salts NH₄C₃H₁N₂O, and AgC₃H₂N₂O,

Methylderivative of the methyl ether $C_6H_2(NO_2)_2(OMe) CO_2Me$ [69°] Prisms (Sal kowski, A 173, 43)

Methyl derivative of the ethyl ether C₆H₂(NO₂)₂(OMe) CO₂Et [47°] Tables

Ethyl derivative of the methyl ether $C_6H_2(NO_2)_2(OEt)CO_2Me$ [80°] Prisms

Ethyl derivative of the ethyl ether C₆H₂(NO₂)₂(OEt)CO₂Et [49°] Prisms

 \mathbf{D} i nitro p oxy benzoic acid

 $C_6H_2(NO_2)_2(\bar{O}H)(CO_3H)$ [5 3 4 1] [237°] Formed by boiling di nitro p-amido benzoic acid with potash (Salkowski, A 173, 36) Thin tables -S 7 at 16 5° — K₂C₇H₂N₂O₇2aq S 32 at 16 5° — BaC₂H₂N₂O₇5aq — BaC₇H₂N₂O₇3½aq — Ag'A — Ag C,H,N2O,

EthylYields ether EtA' [87°]

KC,H,N,20,, S 9, and AgC,H,N,20, Methyl derivative C,H,(NO₂)₂(OMe)CO₂H Dimitransic acid [182°] Formed by nitration of nitro anisic acid (Salkowski a Rudolph, B 10, 1254, Stöhr, A 225, 86) —KA'aq —AgA'

Ethylether EtA' [79°]
Ethyl derivative of the ethyl ether C₆H₂(NO₂)₂(OEt) CO₂Et [59°] Needles

Tri nitro m oxy benzoic acid $C_6H(NO_2)_*(OH) CO_2H$ Formed by warming m diazoamide benzoic acid with HNO3 (Griess, A 117, 28), and by the action of fuming HNO, on m amido benzoic acid (Beilstein a Geitner, A 139, 11) Large crystals (from conc HNO.) (NH₄)₂C₇HN₈O₂2aq Explodes when heated

BaC,HN,O,3aq —Ag,C,HN,3O, Tri-nitro oxy benzoic acid [105°] Formed from m-oxybenzoic acid by successive treatment with dilute H₂SO₄ and HNO₃ (Schardinger, B Tables and prisms (containing aq) 8, 1490) BaC,HN,O,2aq - CaC,HN,O,5aq green needles, exploding at 237°

NITRO-O OXY BENZOIC ALDEHYDE

C₆H₃(NO₂)(OH)CHO [3 2 1] [109°] Formed together with the (5,2,1) isomeride, by nitrating salicylic aldehyde (Mazzara, G 6, 460, Von Miller, B 20, 1927, 22, 1709, Taege, B 20, 2109) Its compound with NaHSO, does not crystallise Sodium amalgam forms brown amorphous $\{C_0H_1(OH)(OHO)\}_2N_2H_2$ (Brigel, A 135, 169) — NaC₁H₄NO₄ — Ba(C,H₄NO₄)₂2aq orange crystals

Acetyl derivative [110°] Phenyl-hydraside [165° Methyl derivative C.H.NO. [1029]. Nitro-o-oxy-benzoic aldehyde acid. C.H. (NO.) (OH) CHO [5.2.1] [125°] Formed as

shove Fo ms a solid compound with NaHSO, -NaA' 2aq needles —BaA', 6aq —BaA', 3aq

Acetyl derivative [112] Phenyl-hydraside [186°]

Msthyl dervative C₆H₄(NO₂)(OMe)CHO
[90°] Formed by nitrating C₆H₄(OMe)CHO
(Schnell, B 17, 1382, cf Voswinckel, B 15, 2027) Needles (from water)

Nitro-m-oxy-benzoic aldehyde

 $C_8H_3(NO_2)(OH)(OHO)$ [2 3 1] [128°] Formed, together with the isomeride [166°], by nitration of m-oxy benzoic aldehyde (Tiemann a Ludwig, B 15, 2052, 3052) Yellow plates, sol benzene

Methyl derivative [107°] (T a L), [102°] $C_6H_3(NO_2)(OMe)CHO$ (R) Formed from the aldehyde, KOH, and MeI (T a L) Formed also, together with the (6, 3, 1) and (5, 3, 1) isomerides from C₂H₄(OMe)CHO and HNO₃ at 0° (Rieche, B 22, 2350) Forms a very soluble compound with NaHSO, With acetone and NaOH it condenses to di methoxy indigo C₆H_s(NO₂)(OMe)CH NOH, its oxim, melts at 170°, and its phenyl hydraz ide C, H, (NO2) (OMe) CH N2HPh at 134

Nitro-m-oxy-benzoic aldehyde

[166°] Formed C₆H₃(NO)(OH)CHO [6 3 1] by nitrating m oxy benzoic aldehyde (T a L)

Needles, v sl sol benzene

Methyl derivative [83°] Plates, vola tile with steam Its compound with NaHSO, is m sol water With acetone and KOH it yields a substance resembling indigo Its oxim C, H, (NO2)(OH)CH NOH melts at 152°, and the corresponding phenyl hydrazide at 154c

Nitro-m-oxy-benzoic aldehyde Methyl derivative C6H3(NO2)(OMe)(CHO) $[5\ 3\ 1]$ [97°] (U), [104°] (R) A product of the nitra tion of [3 1] C₂H₄(OMe)CHO (Ulrich, B 18, 2572, Rieche, B 22, 2354) Does not give the indigo reaction Forms an oxim [148°], and a phenyl hydrazide [126°]

Nitro p oxy benzoic aldehyde $C_6H_3(NO)(OH)CHO$ [3 4 1] [140°] Formed by nitrating p oxy benzoic aldehyde (Mazzira, G 7,285, Herzfeld, B 10,1269) Needles, slightly volatile with steam -C6H3(NO2)(OK)CHOaq -AgA' canary yellow pp

Methyl derivative Nitro anisic alde hyde [84°] Formed from anisic aldehyde, HNO, and H2SO, (Einhorn a Grabfield, A 243, 370) Yellow needles Forms a phenyl hydrazide

[131°]

Di nitro m-oxy benzoic aldehyde Methyl derivative C₆H₂(NO₂)₂(OMe)CHO [110°] Formed, together with an isomeride [155°], by treating [3 1]C₈H₄(OMe)CHO with H₂SO₄ and KNO₃ (Tiemann a Ludwig, B 15, 2055)

Nitro-di oxy benzoic aldehyde Ethyl

derivative C₆H₂(NO₂)(OEt)(OH)CHO[x 5 2 1] Formed from C.H. (OEt)(OH)CHO and [180°] dilute HNO, (Hantzsch, J pr [2] 22, 472)

Scarcely volatile with steam

TETRA-NITRO O-OXY BENZYL ANILINE C₁₂H₈(OH)(NO₂)₄N [66°] Formed from o-oxybenzyl anilne, HNO₂, and H₂SO₄ (Emmerich, A 241, 345) Yellow needles (from benzene) DI - NITRO - DI - OXY DI BENZYL UREA

Dr-ethyl derivative CO(NH CH(OEt) C.H.NO.). [170°] Formed from urea, nutro-benzoic aldehyde, alcohol, and H.SO. (Lüdy, M. 10, 805).

NITRO-OXY-CINNAMIC ACID . NITRO COUMARIO ACID

NITRO - OXY - CUMINIC ACID Methyl derivative C₆H₂(C₄H<sub>7)(NO₂)(OMe)CO₄H
[146°] Formed from the methyl derivative of</sub> cymophenol and dilute HNO, (Paterno a. Canzoneri, G 10, 233) Yellowish crystals — BaA', 21aq

Isomeride v Nitro oxy isopropyl Benzoid ACID

NITRO DI OXY ETHYL PYRIMIDINE

CO < NEt CH SC(NO2) aq Netro-ethyl uracel [1945°] Formed from potassium nitro uracil and EtBr at 150° (Lehmann, A 253, 84) White needles -KA' -AgA' needles, v sl sol cold Aq

DI NITRO OXY - ETHYL QUINOLINE TETRAHYDRIDE Ethylderivative $C_{18}H_{17}N_8O_5$ te $C_9H_7Et(OEt)(NO_2),N$ [77°] Formed by nitrating C.H.Et(OEt)N (Kohn, C J 49, 509, B 19, 1048) Yellow prisms (from alcohol), with basic properties

NITRO OXY MALEIC IMIDE CHANO. The salt NH < CO C NO. separates as lightyellow crystals when a solution of di chloro maleic imide is warmed with KNO2 (Ciamician a Silber, Rend Accad Linc [4] 4, 447, B 22, 33, 2490). It is almost insol water

TETRA NITRO-DI-OXY METHYL-ANTHRA QUINONE C14H3Me(OH)2(NO2)4O2 Tetra netro chrysophanic acid Formed by heating chryso phanic acid with fuming HNO3 (Liebermann a. Yellow plates or needles Gresel, A 183, 175)

NITRO-DI OXY METHYL-ETHYL-PYRIM. IDINE CO $<_{NEt}^{NMe} \stackrel{CH}{CO} > C(NO_2)$ [73°] methyl ethyl uracil Formed from silver nitroethvl uracil and McI at 130° (Lehmann, A 253, Pearly rhombohedra (containing aq)

Nitro-di oxy methyl ethyl pyrimidine

 $CO < NEt CH > C(NO_2)$ [109°] Formed from silver nitro methyl uracil and EtBr at 150° (L). Needles (containing aq)
NITRO-OXY-TRI METHYL-PYRIDINE

 $C_bH_{10}(NO_2)NO$ Nitro methyl ψ lutidostyril [161°] Formed by nitrating oxy tri methylpyridine (Hantzsch, B 17, 1032) Yellow needles or prisms, sol hot alcohol

NITRO-DI OXY METHYL PYRIMIDINE

 $C_{s}H_{s}N_{s}O_{4} \text{ so } CO \underset{NMe}{\stackrel{\mathrm{CH}}{<}} CH \underset{CO}{>} CNO_{2}$ methyl-uracil [255°] S 714 at 20° Formed from potassium nitro-uracil and MeI at 140° (Hoffmann, A 253, 77) Needles (containing aq), v sol hot water Baryta water at 160° liberates methylamine and NH, -KA' needles -BaA', -AgA' minute white needles (from hot water'

Nitro-di-oxy-di-methyl pyramadine

 $CO < NMe CH > C(NO_2)$ [154 5°] From the silver salt of nitro di oxy methyl pyrimidine and MeI at 120° (Lehmann, A 253, 82) Needles (containing aq) Yields NMeH, when heated with baryta at 180°

NITEO-OXY METHYL-QUINAZOLINE

 $O_{\bullet}H_{\bullet}(NO_{\bullet}) < N$ Formed from oxy-=CMe methyl-quinazoline [288°] and conc. HNO, (De

hoff, J pr [2] 42, 348) Yellow crystalline powder, sol alcohol Does not melt below 280°

Methyl derivative [165°] Needles

QUINOLINE $C_0H_1 < N_1 = 0$ Formed by

nitrating oxy (Py 3) methyl quinoline (Conrad a Limpach, B 20, 950) Needles, v boiling alcohol Does not melt at 270°

(B 3) Nitro (B 4) oxy (B 1) methyl quinol-CH CMe C CH CH C(NO₂) C(OH) C N CH [206°] This body is formed by oxidising the corresponding nitroso oxy-methyl quinoline with alkaline K₃F₄Cy₆ (Noelting a Trautmann, B 23, 3667) In the same way may be formed (B 4) nitro (B 1) oxy-(B 2)-methyl quinoline, (B 1) nitro (B 4) oxy-(B 3) methyl quinoline [193°], and (B 2) nitro-

(B 1) oxy-(B 4) methyl quinoline [182°] NITRO-OXY-TRI-METHYL QUINOLINE

NITRO - OXY - TRI - MELINIA CARBOXYLIC ACID C₁₈H₁, N_.O_., ie C₈HMc₃(NO₂)(CO_.H)(OH)N Formed by warm ing (Py 1) oxy (B 1, 2, 4, Py 3) tetra methyl-quinoline with HNO₃ (S G 14) (Conrad a Limnach, B 21, 529) White insoluble powder -NaA' aq yellowish needles

NITRÔ-DI OXY-NAPHTHALENE v NITRO-HYDRONAPHTHOQUINONE

Di-nitro di-oxy-naphthalene Dr ethylderivative C₁₀H₄(NO₂)₂(OEt)₂ [229°] Formed from (\$\epsilon\$)-di chloro di nitro naphthalene and alco [229°] Formed holic potash (Alén, Bl [2] 36, 435) needles

NITRO-OXY-NAPHTHOIC ACID

[**242°**] Formed by $\mathbf{C}_{10}\mathbf{H}_{5}(\mathrm{NO}_{2})(\mathrm{OH})\ \mathrm{CO}_{2}\mathbf{H}$ dissolving its anhydride in alkalis (Ekstrand, J pr [2] 38, 282) Plates — $CaC_{11}H_5NO_55_2^1$ aq yellowish-red needles

 $C_{10}H_s(NO_2) < CO$ Anhydride

Formed by nitrating peri oxy naphthoic acid Yellow needles (from HOAc)

Nitro-oxy-naphthoic acid [202°] (Schmidt a Yields (3)-nitro (a) Burkard, B 20, 2700) naphthol on distillation with lime

NITRO-OXY-(a)-NAPHTHOQUINONE

C₁₀H₅NO₅ te C₆H₄ < CO C NO₂ CO C OH **Nutrona**ph thalic acid [157°] Formed from $\exp{(a)}$ -naphthoquinone, H_2SO_4 , and HNO_5 , the yield being 85 pc of the theoretical (Diehl a Merz, B 11, 1317) Formed also from di chloro (a) naphthoquinone and alcoholic NaNO₂ at 100° (Kehrmann, B 21, 1780, J pr [2] 40, 180) Yellow leaflets or tables—NH, A'—NaA' aq— $KA'aq -BaA'_2 -PbA'$ $aq -PbA'_2 4\frac{1}{2}aq -AgA'$ Sulphonicacid

 $\mathbf{C}_{10}\mathbf{H}_{3}(\mathbf{S}\bar{\mathbf{O}}_{3}\mathbf{H})(\mathbf{NO}_{2})(\mathbf{OH})\mathbf{O}_{2}[2'\ 3\ 2\ 4\ 1]$ Formed di chloro (a) naphthoquinone sulphonic acid [229°] and NaNO₂ (K) $-K_2C_{10}H_8NSO_8$ (dried at 100°) slender yellow needles

DI-NITRO-DI OXY $(\beta\beta)$ DINAPHTHYL DI-SULPHONIC ACID $C_{20}H_a(NO_2)_2(OH)_2(SO~H)_2$ Got by nitrating $C_{20}H_a(OH)_2(SO_3)_2Ba$ (Julius, Chem Ind 10, 97) Yellow needles (containing

o NITRO-p OXY-DIPHENYL

[4 1] $C_6H_4(OH)$ C_6H_4 NO_2 [1 2] [138°] Formed by the action of nitrous acid on the corresponding nitro amido diphenyl (Schultz a Strasser, B 14, 614, A 207, 351) Yellow needles

p Nitro p oxy-diphenyl [4 1] C₄H₄(OH) C₆H₄ NO₂[1 4] [170°| Formed from p mitro p amido diphenyl (S a β)

Nitro oxy-diphenyl C₁₂H₈(NO₂)(OH) Formed by nitration of oxydiphenyl (Latschinoff, J R 5, 52) Lemon yellow prisms (from ether)

D1-n1tro-oxy-diphenyl C₁₂H,(NO₂)₂(OH) [154°] Formed at the same time as the preceding (L) Golden plates (from alcohol) -KA', 2aq sparingly soluble plates

Di nitro di-oxy-diphenyl [3 4 1] $C_sH_s(NO_s)(OH)$ $C_sH_s(NO_s)(OH)$ [1 3 4] [272°] (K), [280°] (S) Formed from pp droxy diphenyl and HNO_s (S G 1 45) (Kunze, B 21, 3331, Schutz, B 21, 3531) Yellow needles, insol alcohol

Di-acetyl derivative [215°] Needles Di-benzoyl derivative [206°] Plates Ethylether [193°] Formed by nitrating the ethyl ether of di oxy diphenyl (Husch, B 22, 336)

 D_1 -nitro-di-oxy-diphenyl $C_{12}H_8N_2O_6$ [184°] Formed by oxidising o nitro phenol with aqueous KMnO₄ (Goldstein, J R 6, 193, 10, 318) Yel low needles (from benzene

Di-benzoyl derivative [191°] Needles Tetra-nitro-di-oxy-diphenyl

[4 3 5 1] C₆H₂(OH)(NO₂)₂ C₆H₂(NO₂)₂(OH) [1 3 5 4] [220°] (K), [225°] (S) From di-oxy diphenyl, HOAc, and HNO₃ (Kunzc, B 21, 3333, Schutz, B 21, 3532) Yellow needles — Na₂A'' —NaHA'' brownish red needles Di-acetyl derivative [236°]

Hexa-nitro tetra-oxy-diphenyl C₁₂H₄N_eO₁₀ xa nitro diresorcin Formed by warming Hexa nitro diresorcin tetra acetyl diresorcin with fuming HNO, (Bene dikt a Julius, M 5, 178) Yell ploding at 230°, v e sol water Yellow crystals, ex-

m NITRO a OXY PHENYL ACETIC ACID v

NITRO MANDELIC ACID
NITRO OXY PHENYL AMIDO BENZOIC ACID $C_6H_4(OH) NH C_6H_3(NO_2) CO H[4 3 1]$ [261°] Formed from bromo nitro benzoic acid, alcohol, and amido phenol at 120° (Schopff, B 22, 3288) Small needles, m sol water

DI NITRO O OXY DIPHENYLAMINE [2 1]C₆H₄(OH) NH C₆H₃(NO₂)₂[1 2 4] [199°] Got from C₆H₃Br(NO₂)₂ and o amido phenol (Schopff, B 22, 900) Orange crystals (from alcohol)

Acetyl derivative [150°] Ethyl derivative [164°] Needles Red needles. Methyl derivative [1519] Needles

Di-nitro p oxy-diphenylamine Di benzoy lderivative C₁₂H₂(NO₂)₂(OBz)NBz [195°] Got by nitrating C₁₂H₂(OBz)NBz (Philip a Calm, B 17, 2437) Small crystals, sl sol alcohol

Di-nitro-di-oxy-diphenylamine Diethyl derivative C₆H₅NHC₆H(NO₂)₂(OEt)₂ [133°] Formed by heating aniline with the diethyl derivative of di nitro hydroquinone (Nietzki, A. 215, 157) Red needles (from alcohol)

NITRO-OXY-PHENYL-ANGELIC-(B) LACT-[4 1] $O_6H_4(NO_2)$ CH CH CH $< \stackrel{\dot{CH}_2}{O} > CO_6$ [111°] Formed by adding soda to a cold solution of C₆H₄(NO₂) C₂H₃Br CH< CH₂>CO (Einhorn a. Gehrenbeck, B 22, 47, A 253, 870)

o-NITRO-β-OXY PHENYL BUTYLENE DI-CARBOXYLIC ACID

[1 2]C₆H₄(NO₂) CH CH CH(OH) CH(OO₂H)₂

[269°] Formed by heating malonic acid (10 g) with o-mi-ro cinnamic aldehyde (15 g) at 125° (Einhorn) A 253, 375) Stellate needles

NITRO-OXY-PHENYL-CARBAMIC ETHER Ethyl derivative CgH3(NO2)(OEt) NH CO2Et Formed, as well as two di nitro- derivatives [141°] and [121°] and a tri nitro derivative [212°] by the action of nitric acid on [4 1]C₆H₄(OEt) NH CO₂Et (Köhler, J pr [2] 29, 261) All four compounds crystallise from alco hol in needles

NITRO DI OXY PHENYL CROTONIC ACID

Anhydride CoH (NO)(OH) COH CO (β) methyl umbelliferone Formed, as well as the di nitro derivative [220°] by nitration of (β) methyl umbelliferone dissolved in HOAc (Pechmann a Cohen, B 17, 2136) Both com pounds crystallise in yellow needles, sol alcohol

NITRO - OXY - PHENYL - ETHYLENE

NITRO OXY STYRENE

o NITRO β OXY PHENYL ETHYL METHYL KETONE

C₁₀H₁₁NO₄ re C₆H₄(NO₂) CH(OH) CH₂ CO CH₄ [69°] Formed from o nitro benzoic aldehyde, acetone, and dilute aqueous NaOH (Baeyer a Drewsen, B 15, 2857) Prisms

p Nitro-β oxy-phenyl-ethyl methyl ketone [586] Formed in like manner from p nitio benzoic aldehyde (Baeyer a Becker, B 16, 1969) Crystals Yields nitro styryl methyl ketone on boiling with Ac O Boiling potash forms a compound (C₁₀H₂NO₃)_n [254°] p NITRO \$ OXY PHENYL (Py 3) ETHYL-

QUINOLINE $C_sH_s(NO_s)$ CH(OH) CH, (NC_sH_s) [160°] Formed by heating $(Py \ 3)$ methyl quinoline with p nitro benzoic aldehyde at 120° (Bulach, B 20 2016) Silky needles (from alcohol) -B' H,PtCl_e -B'HNO, white needles DI-NITRO DI o OXY DI PHENYL-HY DRAZINE Di ethyl derivative

 $\{C_6H_3(NO_2)(OEt)\}_3N_2H_2$ [202°] Formed by reduction of the corresponding azo compound [285°] by alcoholic ammonium sulphide (Andrew, J pr [2] 21, 325) Yellow pusms, insol cold alcohol Hot HClAq converts it into nitro

amido phenol and {C_aH₃(NO)(Ol·t)} N₂
NITRO OXY-PHENYL-METHYL PYRAZOLE $\mathbf{C}_{10}\mathbf{H}_{3}\mathbf{N}_{8}\mathbf{O}_{8}\quad\text{2 }c\quad\mathbf{C}_{6}\mathbf{H}_{5}\;\mathbf{N} \begin{matrix}\mathbf{CO}\;\mathbf{CH(NO_{2})}\\\mathbf{N}&\mathbf{CMe}\end{matrix}$ [127°-

130°] Formed by the action of nitrous acid on oxy phenyl methyl pyrazole, and of nitric acid on the oxim thereof (Knorr, A 238, 187) Prisms (from alcohol), insol acids

NITRO-OXY-PHENYL-PROPIOLIC

Methyl derivative

 $C_6H_3(NO_2)(OMe) C C CO_3H$ [135°] Formed from C.H. (NO2) (OMe) CHBr CHBr CO2H and alcoholic potash (Einhorn a Grabheld, A 243, White needles, sol waterNITRO-OXY-PHENYL PROPIONIC

ACID [8 4 1] $C_0H_3(NO_2)(OH) CH_2CH_2CO_2H$ hydro p-coumaric acid [91°] Formed by nitrating p oxy phenyl propionic acid (Stöhr, A

225, 57) Orange needles (from water)

Methyl ether MeA' [64°] Ne Methyl ether MeA' [64°] Needles Ethyl ether EtA' [38°] Needles Nitro a oxy-phenyl-propionic acid

C₆H₄(NO₂) CH₂ CH(OH) CO₂H. A mixture of the o- and p- isomerides is formed by the action of fuming HNO, at -5° on α -oxy phenyl pro Vol III

pionic acid (Erlenmeyer a Lipp, A 219, 228) The nitrate C₆H₄(NO₂) CH₂ CH(ONO₂) CO₂H of the p isomeride crystallises from hot water in needles, leaving that of the o compound in so-

o-Nitro-\$-oxy-phenyl-propionic acid C9H9NO3 ve [2 1] CoH4(NO2) CH(OH) CH2 CO2H [126°] Formed by oxidation of the product of conden sation of o-nitro benzoic aldehyde with acetie aldehyde (Baeyer a Drewson, B 16, 2206) Formed also from \$\beta\$ bromo o nitro phenyl pro pionic acid and hot Na₂CO₂Aq (Einhorn, B 16, 2214, 17, 1660, 2013) Monoclinic prisms (from water) Dilute H₂SO₄ at 190° converts it into o-nitro cinnamic acid -BaA', 2aq needles

Methyl ether MeA' [51°]

 $C_6H_4(NO_2)$ $CH < {CH_3 \choose O} > CO$ B Lactone [124°] Formed from C_eH₄(NO₂) CHBr CH₂ CO₂H and cold aqueous Na₂CO₃ Yellow monoclinic and cold aqueous Na CO crystals (from chloroform) Split up by boiling with water into o nitro styrene and CO. Boiling HOAc yields indigo

Amide C,H10N2O4 $[197^{\circ}]$ Formed from B bromo o nitro phenyl propionic acid and am monia Formed also from the lactone and NH, (Einhorn, B 16, 2646, Basler, B 17, 1494) Needles, v sol water Yields with Ac O an Needles, v sol water acetyl dcrivative CoHoAcN2O4 [142°], a compound C_sH_sN O_s [c 80°], and the acetyl derivative thereof C_sH AcN₂O₃ [172°]

m-Nitro-β-oxy-phenyl propionic acid 3 1] C, H, (NO) CH(OH) CH, CO H Formed by boiling β bromo m nitro phenyl propionic acid with water (Prausnitz, B 17, 596, 1660) Plates (from water)

[56°] Ethyl ether EtA' Civstals Deposited from Lactone C₉H,NO, [98°] a cold solution of the sodium salt Yields m nitrostyrene on boiling with water

p-Nitro- β -oxy phenyl-propionic acid \tilde{I}_aNO , [132°] Formed by the action of C.H.NO. alkalison β bromo p nitro phenyl propionic acid, its lactone being the intermediate product (Basler, B 16, 3004, 17, 1494) Needles, m sol cold Aq

Methyl ether MeA' $[74^{\circ}]$ Prisms [46°] Crystalline Ethyl ether EtA' Yields p nitro. Lactone C,H,NO, [92°]

styrene when boiled with HOAc

Amide C9H10N2O4 [166°] Prisms (from Forms with Ac2O an acetyl derivative alcohol) [146°-150°]

Anilide C₁₅H₁₄N₂O₄ [176°] Plates

p-Nitro $\alpha\beta$ -di-oxy-phenyl-propionic acid $C_sH_sNO_s$ is $C_sH_s(NO_s)$ CH(OH) CH(OH) CO₂H [168°] Formed from p nitro phenyl glyculus acid and diluted H.SO. (Lipp, B 19, 2645). Plates, sl sol cold water

o Nitro $m\beta$ di oxy phenyl propionic acid Methyl derivative

[2 5 1] C₆H₃(NO₂)(OMe) CH(OH) CH₂ CO₂H [106°] Got from C₈H₃Cl(NO) CH(OH) CH₂ CO₂H and NaOMe (Eichengrun a Einhorn, B 23, 1491) Colourless plates (from water)

an-Di-nitro-8-oxy-phenyl-propionic acid.

Methyl derivative C₆H₄(NO₂) CH(OMe) CH(NO₂) CO₂H Methyl ether MeA' [118°] Formed from methyl ap di-nitro cinnamate by boiling with MeOH (Friedlander a Mahly, B 16, 851, A 229, 210).

QΩ

[77°]. Formed in like Ethyl ether EtA' manner, using EtOH

Ethyl derivative

C₆H₄(NO₂) CH(OEt) CH(NO₂) CO₂H Methyl ether MeA' [110°] Formed by boiling ap dinitro-cinnamic ether with alcohol Monoclinic prisms $a b c = 849 \ 1 \ 517$, $\beta = 87^{\circ} 25'$ Sol potash Yields the salts $Ba(C_1H_1N_2O_1)_2$ and AgC₁₂H₁₃N₂O₇. Ethyl ether EtA' [52°]. Monoclinic crystals

Di-nitro-oxy-phenyl-propionic acid C,H,N,O, [5 3 4 1] C₆H₂(NO₂)₂(OH) CH₂CH₂CO₂H Di nitro hydro p-coumaric acid [138°] Formed by nitrating oxy phenyl propionic acid (Stöhr, A 225, 68) Trimetric prisms (from HOAc) — NH_4HA'' [230°] - $(NH_4)_2A''$ - AgHA'' - Ag_2A'' dark red needles

Methyl ether MeA' [87°] Needles Yields AgMeA" on adding Ag₂CO₂ to its ethereal

Ethyl ether EtA' [175°] Yields red

needles of AgEtA"

Methyl derivative C_eH₂(NO₂)₂(OMe) CH₂ CH₂ CO₂H [124°] by saponifying its methyl ether with H.SO, and HOAc Needles or plates (from dilute alcohol)
Methyl ether C_eH₂(NO₂)₂(OMe) C₂H₄ CO₂Me
[58°] From the basic silver salt and MeI Ethyl ner EtA' [71°] Ne Ethyl derivative ether EtA' Needles, v sl sol Aq

C_cH₂(NO₂)₂(OEt) CH₂ CH₂ CO₂H [126°] Needles Methyl ether MeA' [36°] Ethyl ether Ethyl ether [50°] Needles or plates

Di-nitro oxy-phenyl-propionic acid CoHaN2O, Dinitromebilotic acid [155°] Formed by nitrating melilotic acid (Zwenger, A Suppl 5, 118)
Prisms (from alcohol) —BaA" aq —Ag_sA"

Two isomeric acids are obtained by nitration of phloretic acid (Hlasiwetz, A 102, 155) Both

form yellow crystals

o-NITRO-β-OXY-PHENYL PROPIONIC

ALDEHYDE C.H.NO. 1 e

[12] CaHa(NO2) CH(OH) CH2 CHO Formed from o-nitro benzoic aldehyde, acetic aldehyde, and 2 p c aqueous NaOH (Baeyer a Drewsen, B 16, Crystalline Forms a compound with aldehyde C₅H₅NO₄(C_.H_.O) [125°], which yields indigo on treatment with alkalis Similar compounds of the formula $C_0H_0NO_4(C_2H_4O)$ are formed by the action of m- and p nitro benzoic aldehydes on aldehyde and NaOĤAq The m compound gives off aldehyde at 100°, the p-compound melts at about 115° (Göhring, B 18, 372, 720)

m-NITRO-\$-OXY-PHENYL-PYROTARTARIC Lactone C, H, NO, 1.6

C_cH₄(NO_s) CH

CH(CO_sH)>CH₂ Nitro-phenyl-paracons acid [171°] Formed by heating m nitro benzoic aldehyde with sodium succinate and Ac₂O at 125° (Salomonson, R T C 6, 1) Crystalline Boiling with NH, Aq and BaCl, ppts C₁₁H_{*}BaNO_{*}. Phenylhydrazine at 130° forms C₁₁H_{*}NO_{*}(N₂HPh) [182°] — Cu(C₁₁H_{*}NO_{*})₂, — PbA'₂ needles (from hot water)

Methylether MeC,1H,NO. Oil.

p-Nitro-β-oxy-phenyl-pyrotartarie Lactone [163°] (S), [155°] (Erdmann, B 18, 2742) Formed in like manner from p-nitrobenzoic aldehyde. Boiling with NH, Aq and BaCl₂ ppts. BaC₁₁H₂NO₂—CuA'_2—AgA'.

NITRO-p-OXY-PHENYL-QUINOLINE

C₁₈H₁₀N₂O₃ [151°] Formed in small quan tities when p amido (Py 3) phenyl-quinoline is heated with KNO₂ (Weidel, M 8, 138) Yellow plates, m sol alcohol

m Nitro-(B 2) oxy (Py 1) phenyl-quinoline Methyl derivative

by heating m nitro cinnamic aldehyde with p anisidine and HClAq (Miller a Kinkelin, B 20, Needles (from benzene), sl sol alcohol. (Py 1,4,2)-Nitro oxy phenyl isoquinoline

C15H10N2O3 16 C6H4 C(OH) CPh Formed by passing nitrous acid gas through a solution of oxy phenyl isoquinoline in HOAc (Gabriel, B 19, 831) Small yellow crystals

Methyl derivative C₁₃H, MeN.O. [169°] DI NITRO DI OXY-DI-PHENYL SULPHONE $C_{12}H_8N_2SO_8$ ie $SO_2\{C_6H_3(NO_2)(OH)\}_2$ Formed by nitrating di oxy di phenyl sulphone (Glutz, A 147, 59) Scales, insol water, sol alkalis Yields C₁₂H₆Na₂N₂SO₈ and C₁₂H₄Ag₂N₂SO₈, a dimethyl derivative C₁₂H₆Me₂N₂SO₈ [215°], a diethyl derivative [192°], and a di isoamyl deriva tive [151°] With aniline it forms the compound C12H6(NHPh)2(NO2)2SO2, crystallising from aniline in red prisms

Tetra nitro di-oxy-di phenyl sulphone SO₂{C₆H₂(NO₂),(OH)}₂ [253°] Formed by further nitration of the preceding body (Annaheim, B 11, 1668) Le K_2A'' —Na₂A'' octahedra Long yellow needles -

TETRA NITRO DI OXY DIPHENYL DISUL PHONIC ACID {C₆H(NO₂)₂(OH) SO₃H}₂ Formed by nitration (Limpricht, A 261, 336) -Na A" aq K2A" yellow crystals

m NITRO p OXY-DI-PHENYL THIO-UREA [3 1] $C_6H_4(NO_2)$ NH CS NH $C_6H_4(OH)$ [1 4] [152°] Formed from m nitro phenyl-thiocarb imide and p amido phenol (Steudemann, B 16, Needles, sl sol ether

DI NITRO OXY PHENYL UREA C,H,N,O, netro phenol Formed by heating urea with di nitro amido phenol (picramic acid) (Griess, J pr[2] 5, 1) Plates (from water) —AgA' pp Methyl

NITRO DI-OXY-PHTHALIC ACID $C_nH(OMe)(OH)(NO_2)(CO_2H)_2$ derivative [4 3 6 2 1] Normethylnitrohemipic acid [220°] Formed by boiling its imide with KOH (Elbel, B 19, 2310) White needles, v sol water

 $C_eH(OMe)(OH)(NO_2) < C(NH) > 0.$ Imide [252°] Formed by boiling the oxim

C_sH(OMe)(OH)(NO₂)(CO,H)CH NOH with HOAc Yellow needles, sol hot water and alkalis

Dimethyl derivative v Nitro Hemipio ACID

Di-nitro oxy phthalic acid

C_sH(NO₂)₂(OH)(CO₂H)₂. Juglonic acid Formed by oxidation of juglone or its acetyl derivative by boiling with HNO,

Salts $-A''(NH_t)_2$ reddish yellow tables or thin needles, v sol water $-A'HK - A'Ba \times$ yellow tables (Bernthsen a Semper, B 18, 210) NITRO-OXY-ISOPROPYL-BENZOIC ACID CMe₂(OH) C₄H₄(NO₂) CO₂H [4 8 1]. [191°] Formed by oxidising nitro-cuminic acid or nitro-

cuminol with KMnO, (Widman, B 15, 2549; 16,

2567, 2., 2232) Long needles (from water) — NH₄A' 2rq — CaA'₂.—BaA'₂6aq — PbA'₂5aq — CuA'₂1¹/₃aq — AgA' ¹/₃aq crystals, m sol hot Aq Acetyl derivative [1382]

Ethylether EtA'

Nitro oxy isopropyl benzoic soid [168°] $CMe_2(OH) C_{\bullet}H_{\bullet}(NO_2)CO_2H [4 2 1]$ Formed by oxidising nitro cymene or the scid C.H.Pr(NO₂) C.H. CO.H. with alkaline KMnO. (Widman, B 19, 270, Söderbaum, B 21, 2128) Tables (from ether), m sol hot water

Isomeride v Nitro oxy-cuminic acid

from ethylidene phthalide and NO_2 (Gabriel, B19, 838)

838) Colourless needles (from alcohol)
NITRO - β - ΟΧΥ - p - ISOPROPYL - PHENYL-PROPIONIC ACID

[4 2 1] C_sH_sPr(NO_s) CH(OH) CH, CO_sH [120°] Formed by boiling CoH, Pr(NO2) CHBr CH2 CO2H with aqueous Na₂CO₂ (Einhorn a. Hess, B 17, 2024) Silvery plates

Amide C12H16N2O4 [150°]

Anhydride C₆H₂Pr(NO₂) CH< CH₂>CO

[73°] Formed by the action of cold aqueous Na,CO, on bromo nitro cumyl propionic acid Crystals, v sol alcohol

NITRO DI OXY PYRIMIDINE C.H.N.O. te $co <_{NH}^{NH} CH > c No_r$ Nitro uracil Formed by heating the h sair of 130° (Behrend, A 229, 35, 240, 8) Yellow 130° (Behrend, A 229, as yelds isoby heating the K salt of its carboxylic acid at barbituric acid on reduction Urea forms crys talline $C_1H_1N_3O_3$. Guanidine gives a similar salt $C_2H_1N_3O_4$ aq —KA'aq prisms, sl sol water — CaA'_2 6aq — BaA'_2 5aq — ZnA'_2 8½aq — CuA'_2 7CuO

Nitro-dı oxy pyrımıdıne carboxylıc acıd C₃H₃N₃O₆2 e CO NH C(CO₂H) C NO₂ Formed

by warming di oxy methyl pyrimidine (methyl uracil) with H₂SO₄ and HNO₅ at 80° (Behrend, A 229, 32, 240, 4, Köhler, A 236, 32) Yellow crystals (containing 2aq) —KHA"aq plates, s sol water —BaA" kaq —Ag,A"aq —PbA" 1kaq Ethyl ether EtHA" [250°] Prisms plates, sl

(a) NITRO (Py 3)-OXY-QUINOLINE I_eN₂O₂ 'a'-Netro-carbostyrel Form C.H.N.O. 'a'-Nitro-carbostyril Formed by heating 'a'-nitro o amido cinnamic acid with HClAq at 150° (Friedlander a Lazarus, A 229, 243) Needles (from alcohol) Does not melt below 220°

(β) Nitro (Py 8)-oxy quinoline [260°] Formed in like manner from 'B' nitro amidocinnamic acid (F a L) Needles (from HOAc)

 (γ) Nitro- $(Py \ 8)$ oxy quinoline [280°] Formed by nitrating carbostyril (F. a. L) Needles (from HOAc)

Methyl derivative [181°]. From the silver salt and MeI (Feer a Königs, B. 18,

[168°]. Formed from CH C(NO₂) C-N C OH di-methyl o-mitro-commarinate and alcoholic NH, the resulting (3, 2, 1)-nitro amido-cinnamic amide being heated with HClAq at 140° (Miller

a Kinkelin, B 22, 1711) Prisms, v sol hot water

(B 4, 2) Nitro-oxy quinoline

C(OH) CH C CH CH CH C(NO₄) C N CH [136°] Formed by nitra ting $(B\ 2)$ oxy-quinoline (Skraup, $M\ 3,551$) and by the action of nitric acid on $(B\ 2)$ -oxy-quinoline me carboxylic acid (Schmidt a Altschul, B 20, 2697, 21, 2255) and on nitroso oxy-quinoline (Matheus, B 21, 1642, 1886) Yellow needles -

B'HNO, aq orange prisms, v sol hot alcohol
Nitro-(B 4) oxy-quinoline [173°] Formed
by heating its carboxylic acid with glycerin at 200° (Schmitt a Engelmann, B 20, 2693) and by the action of HNO, (S G 138) on nitroso-(B4)-oxy-quinoline (Von Kostanecki, B24, 154) Needles, sl sol alcohol

Nitro-(B 3) oxy quinoline [255°] Formed by nitrating m oxy-quinoline (Skraup, M Yellow plates, decomposed by fusion

Nitro-oxy quinoline Formed by the action of HNO, on a syrupy acid obtained by oxidation of cinchonine (Weidel a Hazura, M 3, 773) Crystalline powder, melting far above 300°-

B'₁H₂PtCl₂ monoclinic prisms
(B 1, 3) Di nitro (B 4) oxy-quinoline
CH C(NO₂) — C CH CH
C(NO₂) C(OH) C N CH
(276°) Form Formed by the action of HNO, on o oxy quinoline carb oxylic acid, and on ana nitroso o oxy quinoline (Schmitt a Engelmann, B 20, 2692, Kostanecki, B 24, 155, of Bedall a Fischer, B 14, Plates

NITRO-(B 4) OXY-QUINOLINE CARBOXY-LIC ACID C,H,(NO,)N(OH)(CO,H) Formed by boiling the nitrate of o oxy quinoline carboxylic acid with HOAc (Schmitt a Engelmann, $B^{20}, 2693)$ Needles, sl sol HOAc

NITRO-OXY-QUINONE Carbonyl derivative (C₆H_{O2}(NO₂)O)₂CO [260°] Formed by oxidation of nitro amido phenyl carbonate by chromic acid mixture (Lowenberg, C C. 1886, 390) Pale brown needles

Nitro-di-oxy quinone

CO C(OH) C(NO) CO Formed by warming nitro di imido resoicin with dilute (10 pc) NaOHAq (Nietzki a Schmidt, B 22, 1659) Golden needles, m sol water - K2A" orange needles

Di nitro di-oxy quinone

 $CO < C(NO_2) C(OH) > CO$ Nitranilio acid.

Formation -1 By the action of nitrous acid on hydroquinone (Nietzki, B 10, 2147) -2 By the action of a mixture of fuming HNO, and conc H2SO4 on di acetyl hydroquinone below -5° , the yield in this case being 65 pc (Nietzki, B 16, 2092, 18, 499) -3 By adding dinitrohydroquinone to a cooled mixture of HNO, (3 pts) and HOAc (6 pts) (Nietzki, A 215, 142) -4 By boiling s di-nitro-di-amidoquinone with dilute potash (Nietzki, B 20, 2116) -5 By the action of fuming HNO, on CO₂H C<CO C(OH)<CO CO₂H (Hantzsch, B 19,

2398, cf Loewy, B 19, 2385)
Preparation—By slowly adding a hot saturated alcoholic solution of chloranil (4 pts) to a concentrated aqueous solution of sodium nitrite (10 pts.) heated to 80°-90°, a yellow crystalline

pp of the sodium nitranilate soon separates. and a small quantity which remains in solution is precipitated by NaOH, the whole is recrystallised from hot water (Nef, B 20, 2027)

Properties -Golden tables, v sol water and alcohol, insol ether When anhydrous it explodes at 170° without previous fusion FeCl, gives a green crystalline pp Chlorine forms exalic acid and chloropicrin (Levy, A 249, 66) On reduction it yields tetra oxy di amido benzone which gives p phenylene diamine on distillation with zinc-dust (Nietzki, B 19, 2727) Hydroxylamine hydrochloride forms an explo Salts — Na₂A" dichroic monoclinic crys

tals, a b c = 9461 985, $\beta = 87^{\circ} 51' - K_2A''$ yellow needles (from hot water) -(NH₄)₂A" -

BaA" plates, insol water

A product of the Di-nitro-di-oxy-quinone action of nitrous acid on protocatechuic acid dissolved in ether (Gruber, B 12, 519) Greenishyellow needles, v sol water -Na₂A" 2aq plodes when heated

NITRO-OXY STYRENE Methyl derivative [124] C₈H₃(OMe)(NO₂) CH CH₂ [89°] Formed, together with the di nitro derivative C₈H₃(OMe)(NO₂)₂ C₂H₃ [163°], by the action of cone HNO₃ on [41] C₈H₄(OMe) CH CH CO₂H (Einhorn a Grabfield, A 243, 366) Crystals, volatile with steam Yields a dibromide [79°] Forms, on oxidation, nitranisic acid [187°

NITRO-OXY-STYRYL METHYL KETONE

Methyl derivative CuHuNO, 16 [4 3 1] C₆H₃(OMe)(NO₂) CH CH CO CH₃ Formed by nitration of the ketone, and also by condensation of C₆H₃(OMe)(NO₂)CHO with ace tone (Einhorn a Grabfield, A 243, 364) Yellow needles (from water), sol ether

NITRO-OXY SULPHO BENZOIC ACID C,H,NSO, 26 $C_8H_2(NO_2)(OH)(SO_3H)(CO_2H)$ Formed from nitro-o oxy benzoicacid and fuming H_2SO_4 (Mandt, B 10, 1701) $-Ba_3A'''_2$ 12aq hair-like needles

NITRO OXY TOLUENE v NITRO CRESOL Nitro-di oxy-toluene v Nitro-orcin

CaMe(NO2)(OH) Nitro-tetra oxy toluene [157°] Formed by the action of HCl and SnCl, onnitro-di oxy-toluquinone (Kehrmanna Brasch, J pr [2] 39, 382) Black needles, forming a violet powder Its solution forms HCy, oxalic acid, and other products on boiling

Di nitro di-oxy-toluene

C_eHMe(NO₂)₂(OH)₂[1 3 5 2 4] D₄-nitro cres orcin [90°] Formed from cresorcin and HNO₅ (Von Kostanecki, B 20, 3136) Needles, m sol cold water

NITRO-OXY-o TOLUIC ACID C. H., NO. 1 e $C_6H_2Me(OH)(NO_2)CO_2H[1 4 x 2]$ [172°] Formed by nitration of oxy o toluic acid (Kostanecki a Niementowski, B 18, 254) Needles, sol hot Aq

Nitro oxy-m-toluic acid C₆H₄Me(OH)(NO₂) CO₂H[3 4 5 1]? [87°] Formed by heating (4,8,1)-oxy toluic acid with conc HNO₂ (Mahon, Am 4, 186) Yellow needles, sl sol water Its salts explode when heated -CaA', 4aq -BaA', 4aq orange needles; crimson

when anhydrous

Nitro-oxy-p-toluic soid C_cH₂Me(OH)(NO₂) CO₂H[4 3.x 1] [188°]. Formed by the action of nitrous soid on (8,4,1) amido-

toluic acid (Ahrens, Z 1869, 105) Golden

needles —BaA'₂7aq scarlet, al sol alcohol Nitro-oxy tolunc acid Methylder watwe C_sH₂Me(OMe)(NO₂)CO₂H [175°] Formed from the methyl ether of thymol and dilute HNO, (Paterno a Canzoneri, G 9, 445) needles, v sol alcohol -BaA'2 2aq coloured crystals

Ethyl derivative [162°] Formed, in like manner, from the ethyl ether of thymol. Long

slender needles

Nitro w oxy o toluic acid

C₆H₃(NO₂)(CH₂OH)CO₂H[4 2 1] [129°] Formed by dissolving nitro phthalide in aqueous KOH (Hoenig, B 18, 3451) Minute needles —AgA'

Tri nitro oxy m-toluic acid

C_eHMe(OH)(NO₂)₃CO₂H[1 3 2 4 6 5] Nitrococcic

acid [170°-180°] Formed by the action of boiling nitric acid (SG 137) on cochineal (De la Rue, A 64, 23, Liebermann a Dorp, A 163, 100) and on (5,3,1) oxy toluic acid (Kostanecki a Niementowski, B 18, 250) Colourless plates (containing aq) On boiling with moist Ag₂O it yields silver trinitro cresol and CO₂—(NH₄), A" ½aq —BaA'₂aq —Ag₂A" needles NITRO OXY m TOLUIC ALDEHYDE

C₆H,NO₄ ie C₆H,Me(NO₂)(OH)CHO [5 3 2 1] [141°] Formed by warming oxy toluic aldehyde with HNO₃ (Schotten, B 11, 788) Yellow needles, sl sol hot water

Nitro oxy m toluic aldehyde

C_eH₂Me(NO₂)(OH)CHO [5 3 4 1] [152°] Formed by nitrating (4,3,1) oxy toluic aldehyde (S) Needles, sl sol hot water

NITRO DI OXY TOLUQUINONE

 $C_6Me(NO_2)(OH)_2O_2$ [2 5 3 6 4 1] Toluntranılıc acıd [180°] Formed by the action of a dilute acid [180°] alcoholic solution of KNO on trichloro tolu quinone (Kehrmann, B 21 1779, J pr [2] 39, 377) Golden needles (containing xaq) Its aqueous solution decomposes on boiling forming HCy, oxalic acid, and CO _K2A" day yellowish red prisms

ĎI NITRO DI OXY DITOLYL C, H, N,O, [273°] (G), [270°] (D) Formed by boiling tetrazo ditolyl sulphate with HNO₃ (Gerber, B 21, 750), by the action of nascent nitrous acid on di amido ditolyl (the yield being quantitative), and by heating di oxy ditolyl di carboxylic acid with HNO₂ (Deninger, J pr [2] 40, 300, B 21, 1639) Yellow needles (from toluene or pyridine)

NITRO - OXY - TOLYLENE ETHENYL AMIDINE C.H., N.O. [256°] Formed by the action of alcoholic ammonium sulphide on the acetyl derivative of di nitro p toluidine (Bankie vitch, B 21, 2404) Lustrous green needles, not affected by HClAq at 200°

NITRO-PENTANE C.H,1NO, 2 e Pr CH₂ CH₂ NO₂ (150°-160°) Formed from isoamyl iodide and AgNO, (V Meyer, B 5, 203,

A 171, 43, 175, 135)

Di nitro pentane C,H, CH(NO2), Formed from di amyl ketone and HNO_s (Chancel, C R94, 399) Heavy oil Forms n-valeric acid on reduction —KC₃H₃N₂O₄ —AgA'
o NITRO-PHENOL C₃H₄NO₃ t e

C.H.(NO.) OH [1 2] Mol w 189 [45°] (214°) S V S 107 64 (Schiff)

Formation -1 Together with the p isomeride by nitration of phenol (Hofmann, A 103, 347; Fritzsche, A 110, 150, J pr 73, 293, Gold

stein, B 11, 1943) —2 By heating o bromonitro benzene [38°] or o chloro nitro benzene with aqueous potash in sealed tubes (Zincke a Walker, B 5, 117, Engelhardt a Latschinoff, B 3, 423)—3 By boiling o di-nitrobenzene with NaOHAq (Laubenheimer, B 9, 1828) -4 Together with p nitro phenol by boiling diazobenzene sulphate with nitric acid (Nölting a Wild, B 18, 1338) —5 Together with p nitro phenol by adding liquid N_2O_4 to cooled CS₂ containing C₆H₆ONa in suspension (Schall, B 16, 1901) —6 By heating diazo benzene nitrate with dry toluene, nitrogen being given off (Remsen a Orndorff, Am 9, 390) — 7 By the action of NaNO, and H2SO, on aniline

(Deninger, J pr [2] 40, 298)

Preparation—Phenol (1 pt) is slowly added to a mixture of HNO₃ (1 pt of SG 138) and water (6 pts), cooled to 0°, the product is neutralised with Na₂CO₃ and distilled with water

(Neumann, B 18, 3320)

Properties.-Light yellow prisms or needles, v sol alcohol and ether, sl sol cold water

Reactions -1 Reduced by tin and HCl to o amido phenol -2 Aqueous NH3 (35 pc) at 160° - 200° yields o nitro aniline (Merz a Ris, B 19, 1749) -3 Phenyl hydrazine dissolved in vlene at 100° produces o amido phenol, benzene,

NH., and nitrogen (Barr, B 20, 1497)

Salts -The colour of the salts has been examined by Carnelley a Alexander (C J Proc 4,64) — NH₄A' scarlet plat $s = KA'\frac{1}{2}aq$ orange red crystals (F)—kA'aq (Post, B=8, 1552) S 16 at 6°, 21 at 15°—kA'aq (Post, kA'aq) scarlet plates, v e sol water — Ba A'₂ S 9 at 6° SrA'₂3aq — CaA'₂4aq plates — CaA'₂aq orange needles — AgA' orange red pp S 14 at 15°

Acetyl derivative C, H, (NO) OAc [41°] (253°) Long colourless needles or piisms, v

sol alcohol (Bottcher, B 16, 1933)

Benzoyl derivative C,H,(NO,)(OBz) [59°] Formed from o nitro phenol and BzCl (Hubner, A 210, 386, Schiaparelli, G 11, 73, Neumann, B 18, 3320, 19, 2018) Prisms or needles Yields on intration the compound C₆H₄(NO₂) O CO C₆H₄(NO₂) [1 3] [126°], crystal-

lising in needles

Methyl cther C₆H₄(NO₂)(OMe) o Nitro anisole [9°] (277°) at 735 mm Formed, together with the p isomeride, by nitration of anisole Formed also by methylation of o nitro phenol (Brunck, Z 1867, 204, Muhlhauser, A 207, 237) and by boiling o chloro nitro benzene with NaOMe in HOMe (De Bruyn, R T C 9, 200) Converted into o nitro aniline by heating with ammonia (Salkowski, A 174, 278)

Ethyl ether C.H.(NO2)(OEt) o-Nitrophenetol (267°) Formed by ethylation of o nitro phenol (Groll, J pr [2] 12, 207, Seidel, J pr [2] 42, 448) and by heating C₆H₂Cl(NO₂) with NaOEt (De Bruyn) Oil When distilled with alcoholic potash it yields C₈H₄(NH₂)(OEt) and no azo compound, but when reduced in alcoholic solution by sodium-amalgam it forms $N_2(C_0H_4OEt)_2$ and $N_2O(C_0H_4OEt)_2$ (Schmitt a. Möhlau, J pr [2] 18, 200)

Bromo-ethyl ether $C_0H_4(NO_2)O$ C_0H_4 Br.

[44°] Formed from C.H. (NO.) (ONa) and ethylene bromide (Weddige, J pr. [2] 24, 246). Yellow

prisms (from alcohol)

Reactions -1. With an alcoholic solution of

NH, it yields CoH4(NO2)O C2H4NH2 [78°] and NH(C₂H₄O C₂H₄NO₂)₂ [192°] -2 Heated with potassium salicyhie ether C₄H₄(OK)CO₂Et in alcoholic solution it yields two products:

(a) an ether C₂H₄(NO₂) O C₂H₄ O C₃H₄ CO₂Et [c 100°] saponified by HCl yielding the corresponding acid [145°], which may be reduced to an amido acid [110°] whose hydrochloride melts at 177°, and (b) a compound of the formula $C_6H_4(NO_2) O C_2H_4 O CO_2 C_6H_4OH$ [106°] which gives an acetyl derivative [80°] (Wagner, J pr [2] 27, 212) — 3 Heated with [4 1] C₆H₄(OK)CO₂Et in alcoholic solution it forms o nitro phenoxy ethyl p-oxy benzoic ether [103°] which is saponified by HCl at 140°, forming an acid C₆H₄(NO₂)O C₂H₄ O C₆H₄ CO₂H 162 206°] The corresponding amido acid melts at 185° (Wagner) —4 Potassium benzoate at 140° yields C₆H₁(NO₂) O C₂H₁ OBz [77°]

Amido ethyl ether C₀H₁(NO₂) O C₁H₁NH₂ [73°] Formed as above Small plates (from water) Yields a benzoyl delivative [95°] and a dibenzoyl derivative $C_6H_4(NO_2)$ O C_2H_4 NB7₂ [122°] The benzoyl de rivative reduced by tin and hydrochloric acid yields $C.H_4 < NH CPh > N [151^{\circ}] (Weddige, J pr [2])$ 24, 250)

Lthylene ether C2H4(OC4H4 NO2)2 [163°] Formed from CoH4(NO)ONa and CoH4Br2

Isobutylether (275°-280°) SG 29 1 136 (Riess, B 3, 780)

Benzylether C.H. CH, O.C.H. (NO.) [29° From the K salt and C H,Cl (Kumpf, A 224,

Nitro benzylether $C_b\hat{H}_4(NO_2)$ CH₂ O $C_b\hat{H}_4$ NO₂ [129°] Needles (K)

Phenacyl ether [1180] C,H,(NO2) O CH2CO C,H, (194°)I ormed from the K salt and w bromo acetophenone (Lellmann a Donner, B 23, 172) Needles, m sol alcohol ZnCl, and HCl at 100° convert it into C₆H₄ O CH₁ [103°] crystallising in needles, and forming the salts B'H.PtCl, and B H AuCl,

m Nitro phenol C.H.(NO)OH[13] (194° at 70 mm) Obtained from m nitro-aniline by the diazo reaction (Fittig a Bantlin, B 7, 179, 11, 2099, Henriques, A 215, 323, Wagner, J pr [2] 32, 70) Yellow crystals, sol. hot water, not volatile with steam -KA' 2aq: orange needles S 12 at 6° (Post a Mehrtens, B. 8, 1552) —BaA' 2aq S 17 at 6° —PbA'(OH). 8 013 at 15° —AgA' brownish red pp Bensoyl derivative C₆H₄(NO₂) OBz.

Pale yellow crystals (Neumann, B 19, 2979) Nitric acid (SG 148) converts it into crystalline m nitro benzoyl derivative C.H.(NO.) O CO C.H.(NO.) [129°]

Methyl ether MeA' $(254^{\circ}).$ Needles, volatile with steam (Bantlin)

Ethyl ether EtA' [34°] (2646) (Bantlin,

Wagner, J. pr [2] 32, 71)
Bromo-ethyl ether C₂H₄BrA' Formed, with the following, from the K salt and ethylene bromide (Weddige, J pr [2] 24, 255)

Ethylene ether C₂H,A'₂ [139° p-Nitro-phenol C₆H₄(NO₂) OH. [139°] [114°]. S.V S 108 28 (Schiff).

Formation.-1 Together with the o isomer-

ide, by the nitration of phenol, especially at | low temperatures (Fritzsche, J pr 75, 257, Goldstein, J R. 10, 353)—2 By heating p chloro-nitro-benzene (85°) or bromo nitro-benzene [125°] with aqueous potash at 130° (Engelhardt a Latschnoff, B 3, 423, Richter, B 4, 460)—3 From acetanilide by nitrating, and heating the M 10H NO (NHA) with and heating the [41]C₆H₄(NO₂)(NHAc) with cone NaOHAq (Wagner, B 7, 76)—4 From p-nitro-aniline by the diazo- reaction (Fitting, B , 280) -5 By dry distillation of nitro o oxybenzoic acid (Schmidt a Cook, K 3, 41) 6 By exidation of nitrose phenol (Baeyer, B 7, 965) -7 Together with the o isomeride, by adding liquid N2O4 to cooled CS2 containing C.H.ONa in suspension (Schall, B 16, 1901) -8 By the action of NaNO₂ (in excess) and H₂SO₄ on anline, o ntro phenol being also formed (Deninger, J pr [2] 40, 298)

Preparation—The mixture of o- and p intro-

phenols is distilled with steam The residue is dissolved in hot water and mixed with excess of Na,CO, when C₆H₄(NO₂)ONa crystallises out on cooling (Salkowski, A 174, 280)

Properties — Slender colourless needles (from water Dimorphous (Lehmann, $Z ext{ } K ext{ } 1, ext{ } 45)$ V sol alcohol Not volatile with steam Sol

hot HClAq (Kollrepp, A 234, 1)

Reactions —1 Distillation with PCl, yields p chloro-nitro benzene [85°] —2 Aqueous ammonia at 160° to 200° forms p nitro aniline (Merz a Ris, B 19, 1749) —3 Phenyl hydrazine at 100° produces p-amido phenol, benzene,

NH₃, and nitrogen (Barr, B 20, 1499)

Salts—The colour of the salts has been examined by Carnelley (C J Proc 4, 64)—NaA'4aq yellow tables—NaA'2aq Heat of neutralisation 12,840 (Alexejeff a Werner, Bl [3] 2, 718)—NaHA', 2aq orange red prisms (from water)—KA'2aq S 45 at 6° (Post a Mehrtens, B 8, 1552)—KHA', 2aq—BaA', 8aq monocling prisms S 1 at 6° 12 at 15° 8 1 at 6°, 13 at 15° monoclinic prisms BaH₂A'₄4aq — SrA'₂7aq yellow needles — GaA'₂4aq — CaH₂A'₄8aq — MgA'₂8aq — Pb₅O₂A'₆ — Pb₂HA'₅ — AgA'aq scarlet pp, changing to orange prisms — AgA'2aq S 3 at 15° — AgA'A AgHA'₂aq yellowish green laminæ—Ag₅HA'₆ purple needles

Bensoyl derivative C.H.(NO2) OBz [142 5°] Colourless efflorescent needles (from alcohol) (Schiaparelli, G 11, 73, Neumann, B 19, 2020) On treatment with HNO, (S G 1 48) 1t forms [4 1]C₆H₄(NO₂) O CO C₆H₄NO₂[1 3]

 $[185 5^{\circ}]$

Methyl ether MeA'. [51°] (259°)
Formed by methylation of p nitro phenol (Brunck, Z [2] 3, 202, Willgerodt a Ferko, J pr [2] 33, 152, Skraup, M 6, 761) Formed also by heating p chloro mitro benzene with KOH dissolved in MeOH (Willgerodt, B 14, 2632,

15, 1004)

1004) Prisms
Ethyl ether EtA' [58°] (283°) (Andress, J. pr [2] 21, 831) Formed from the Ag salt and EtI (Fritzsche) and also from C.H.OEt and fuming HNO, (Hallock, Am 1, 271) Obtained also by boiling p-chloro-nitro benzene with KOH and dilute (60 pc) alcohol (Will-geredt B 15 1002) Prepared by besting gerodt, B 15, 1002) Prepared by heating C.H.(NO2)(OK) with KEtSO4 in alcoholic solution for 8 hours (Willgerodt a Ferko, J pr. [2] 83. 158). Prisms Sodium amalgam rapidly re-

duces it, in alcoholic solution, to N₂(C₆H₄ OE1).

(Schmitt a Möhlau, J. pr [2] 18, 199)

Ethylene ether O.H.A. [143°] Formed. at the same time as the bromo ethyl ether, by heating the Na compound with ethylene bromide at 140° (Weddige, J pr [2] 21, 127, 24, 254)

Bromo-ethyl-ether CH₂Br CH₂A' [68°]

Yellowish plates, insol water, v sol alcohol

Yellowash plates, insol water, v sol alcohol Reactions—1 Heated with potassium p oxy benzone ether [4 1] C.H. (OK) CO.Et it forms C.H. (NO.) O C.H. O C.H. CO.Et [181°], which when saponified by HClAq at 180° yields the corresponding acid [218°] (Wagner, J pr [2] 27, 224)—2 Alcoholio [2 1] C.H. (OK) CO.Et forms C.H. (NO.) O C.H. O CO. C.H. (OH [181°] and the ether C.H. (NO.) O C.H. O C.H. (O.H. CO.Et [c 81°] whence HO! liberates the acid [132°]

Amido ethyl ether C,H,(NH2)A' Formed by heating the bromo ethyl ether with alcoholic ammonia Yellow scales (from water)

Isobutyl ether (285°-290°) S G

1 105

Bensylether C.H.CH.A' [106°] Prisms. Yields on nitration a compound melting at 168° (Kumpf, A 224, 123)

p Nitro-bensyl ether [183°] Needles Fourth and fifth nitro-phenols have been de scribed by Fittica (J pr [2] 24, 5, B 13, 711) but their existence has not been confirmed by other chemists (Natanson, B 13, 415)

(a)-Di nitro-phenol C₆H₅(NO₂)₂(OH) [4 2 1] [114°] S 48 at 100°, 5 at 18°, 014 at 0°

(Gruner, J pr 102, 222)

Formation—1 By nitration of phenol, on itro phenol, and p nitro phenol (Laurent, A Ch [3] 3, 212, Körner, Z [2] 2, 663, 731)— 2 From anisole by nitration and saponification (Cahours, A Ch [3] 25, 22) —3 From di nitro amido phenol (picramic acid) by elimination of NH2 (Griess, A 113, 210) -4 From chloro dinitro benzene [50°] and bromo di nitro benzene [72°] by heating with potash (Clemm, J pr [2] 1, 145, Engelhardt a Latschinoff, B 3, 97) — 5 By boiling a tri nitro benzene with aqueous Na₂CO₃ or by heating it with water at 160° (De Bruyn, R T C 9, 191) -6 By boiling i dinitro aniline with KOHAq for a long time (Will gerodt, B 9, 979) -7 From di nitro di ethyl aniline and dilute potash (Van Romburgh, R T C 2, 35)

Properties - Yellowish rectangular plates

(from water), v sl sol cold alcohol

Reactions -1 Yields only picric soid on further nitration (Hubner a Schneider) — 2 Aqueous KCy at 70° forms potassium meta purpurate C,H,KN,O, which separates as brownish red crystals with green lustre (Pfaund ler a Oppenheim, Z 1865, 470, Sommaruga, A 157, 335)

Salts — KA' aq S 14 at 6° (Post a Mehrtens, B 8, 1554), 16 at 7° (Hubner a Schneider, A 167, 92) — KA' aq (Romburgh) — NaA' aq — BaA'₂7aq golden needles—BaA'₂6aq yellow needles—BaA'₂6aq orange prisms S 8 at 7°. —BaA₂4aq monoclinic crystals (P a M)— MgA'₂9aq—MgA'₂12aq—Pb(OH)A'2aq S. 00 at 15°—MnA'₂6aq—NiA'₂8aq—AgA'aq. S 4

Bensoyl derivative O.H.(NO.),OBs. Plates (from alcohol) (Laurent a. Gerhardt, 4.

75, 77).

m Nitro-benzoyl derivative [161°] Formed by nitration of [2 1] C.H.(NO.) OBz or of the prisomeride (Neumann, B 18, 3322, 19,

Needles

Methyl ether MeA' [88°] Formed by boiling anisole or anisic acid with fuming HNO. (Cahours, A 69, 236) or by heating (4, 2, 1)chloro di mitro benzene or i tri mitro benzene with KOH dissolved in MeOH (Willigerodt, B 12, 762, De Bruyn, R T C 9, 190) Needles Ethyl ether Eth' [86°] Formed by the action of HNO, on C.H.OEt (Cahours, A 74,

315) and on $N_1(C_0H_4 \text{ OEt } [1 \text{ 4}])_2$ (Andrew, J particle) [2] 21, 335), and also in the same way as the methyl ether (W) Needles
Allyl ether C,H,A' [47°]

Di-oxy propyl ether C,H,(OH),A' [c 83°] Formed from [1 2 4] C,H,Cl(NO,),glycerin, and KOH (W)

Phenyl ether C,H,A' [71°] (W) Benzyl ether C,H,CH2A' [149°]

p Nitro benzyl ether [201°] (Kumpf)

(β) D₁ nitro phenol C₆H₃(NO₂)₂(OH) [4 3 1] [64°] Formed, together with the (a) isomeride, by nitrating o nitro phenol (Hubner a Schneider, A 167, 89, Salkowski, A 174, 270, Körner, G 4, 325) Pale yellow needles (from water), sl sol water, v e sol hot alcohol Somewhat Somewhat volatile with steam -NaA' 3aq red needles -KA' S 13 at 6° —BaA', aq golden needles S 18 at 7° —MgA', 6aq —Pb,OA', S 037 at 15° —AgA' S 3 at 6° (Post a Mehrtens, B 8, 1552) -AgA'aq red needles

m-Nitro benzoyl derivative [149°] Got trom [3 1] C₆H₄(NO₂)OBz and HNO₂ (Neumann, B 19, 2980) Yellow needles, sl sol ether Methyl ether MeA' [117°] Converted

by NII, Aq at 130° into di nitro aniline [138°] Ethylether EtA' [58°] Needles

Benzyl ether PhCH,A' [76°] Prisms Yields [4 1] $C_8H_4(NO_2)$ CH O $C_8H_3(NO_2)_2$ [1 2 6] [137°] on nitration (Kumpf, A 224, 130)

(γ) Di nitro phenol $C_eH_a(NO_2)$ (OH) [5 3 1] $[104^\circ]$ (B), $[122^\circ]$ (De B) Formed, together with the (5) and (ϵ) isomerides, by nitration of m nitro phenol (Bantlin, B 11, 2103, A 215, 324) Obtained also by heating its methyl ether with conc HClAq at 180° (De Bruyn, R T C

9, 208) Needles, volatile with steam — KA' 2aq
—BaA', 3aq — BaA', 2aq red feathery crystals

Methyl ether MeA' [96°] (B), [105°]
(De B) (above 360°) Formed by heating s trinitro benzene with NaOMe in HOMe for 24 hours

(De Bruyn) Needles

(5) D₁-nitro phenol $C_8H_8(NO_2)_2(OH)$ [4 3 1] [134°] Prepared, together with the (ε)- and (γ)isomerides, by intration of m-nitro phenol (Bantlin, B 11, 2104) Colourless needles, not volatile with steam—BaA', 3aq brown prisms

Methyl ether MeA' [70°] Needles

Methyl ether MeA'

(e) Di-nitro-phenol C.H.N.O. t c. C.H.(NO.).(OH) [8 2 1] [144°] Prepared, together with the (γ) and (δ) isomerides, by nitration of m-nitro phenol (Bantlin, B 11, 2104) Yellow needles (from water) -KA' 2aq yellow needles —BaA', brown needles

Methyl ether MeA' [118°]

Tables Tri - nitro - phenol C.H. (NO.) OH [6 4 2 1]
Provid acid Mol. w 229 [122°] S 626 at 8 626 at 5°; 1 225 at 20°, 8 89 at 77° (Marchand. J

 R_{∞} 78 82 in a 174 pc. benzene pr 64, 91) solution (Kanonnikoff, J pr [2] 31, 348)

Formation -1 By the action of hot nitric acid on phenol, tri-bromo phenol, o and p- nitrophenols, (a)- and (β)- di nitro phenols, saligenin, salicylic aldehyde, salicin, salicylic acid, phlorızın, ındıgo, coumarın, aloes, gum benzoïn, bal sam of Peru, and from the resin of Xanthorrhea hastilis (Hausmann, Journ de Phys et de Chimie, 1788, Welter, A. Ch. 29, 801, Liebig, P. 18, 191, 14, 466, A. 9, 80, 89, 350, Dumas, A. Ch. [2], 53, 178, [3], 2, 228, Laurent, A. Ch. [8], 3, 221, A. 48, 219, Perra, D. P. J. 165, 386, Piria, A. 56, 63, Stenhouse, A. 57, 88, 66, 243, Carey Lea, Am. S. [2], 26, 279, E. Kopp, A. Ch. [20, 12, 12], Palekail, A. A. Ch. [20, 12], Palekail, Palekail, A. Ch. [20, 12], Palekail, Palekail, Palekail, Palekail, Palekail, Palekail, Palekail, P A Ch [3] 13, 233, Delalande, A 45, 337, Mar chand, A 48, 336, 52, 345, Schunck, A 39, 6, 65, 234) —2 By boiling (1,2,4,6)-chloro-tri nitro-benzene (picryl chloride) with aqueous Na₂CO₃ (Engelhardt a Latschinoff, B 3, 98, Clemm, J pr [2] 1, 145) —3 By exidation of s-tri nitro benzene with K-FeCy, in slightly alkaline solution (Hepp, B 13, 2346) —4 By heating iodo benzene with silver nitrite at 150° (Geuther, A 245, 100)

Preparation —Phenol (1 mol) is dissolved in conc H2SO4 and the resulting phenol sulphonic acid treated with HNO, (41 mols of SG 135)

(Schmitt a Glutz, B 2, 52)

Properties - Light yellow lamins (from water) or trimetric prisms (from ether) be sublimed if slowly heated, but if a few milli grammes be dropped into a red hot tube violent detonation occurs, with a larger quantity a less violent decomposition occurs (Berthelot, A Ch [6] 16, 21) Sl sol water, a 01 pc solution being distinctly yellow V sol alcohol and ether Tastes bitter Dyes silk and wool yellow It is poisonous Forms crystalline compounds with aromatic hydrocarbons (Fritzsche, J pr 73, 212, A 109, 247)

Reactions -1 Bleaching pouder yields, on boiling, chloropicrin CCl, NO, and tetra chloro quinone Amixture of KClO, and HCl acts in like manner —2 Distillation with aqueous NaOBr forms bromopicrin (Stenhouse, P M [4] 8, 363) 3 Ferrous sulphate and lime reduce it to di nitro amido phenol (picramicacid) (Girard, C R 36, 421) - 4 Tin and HClAq reduce it to tri amido phenol (picramine) (Roussin, Bl 1861, 60, Beilstein, A 130, 244) Iodide of phos phorus acts in like manner on its aqueous solu tion (Lautemann, A 125, 1) -5 Hot conc KCyAq forms a blood red solution of potassium isopurpurate which crystallises in brownish-red scales with green lustre having either the formula KC, H, N, O, (Hlasswetz, A 110, 289) or KC₈H₂N₅O₅ (Baeyer, J 1859 458) Ammonium chloride converts this salt into an ammonium salt

NH, C, H, N, O, greatly resembling murexide — 6 PCl, yields C, H, Cl(NO), (Pisani, C, R, 39, 852) Salts — Explode when struck or when strongly heated — NH, A' trimetric prisms (Laurent, Rev Scient 9, 26)—LiA' SG 12 1716 slender yellow prisms (Beamer a. Clarke, Am 1, 153) — NaA' S about 8 at 15° S (alcohol) 125 in the cold (Hager, Pharm Centr 22, 225) — KA' Trimetric prisms, a b c = 1270188 (Laurent, Rev Scient 10, 26) S 4 at 15°, 7 at 100° S (alcohol) 04 (Hager) Explodes when struck, giving off CO₂, CO, and

nitrogen, with smaller quantities of hydrogen and CH., and leaving a residue of KCy, carbon, and K₂CO₂(Sartana Vieille, C R 93,61)—BaA'₂5aq monoclinic crystals—BaA'₂6aq S (of BaA'₂) 12 at 17° (Tscheltzoff, A Ch [6] 8, 238)—BaA'₂4aq S 6 at 6° (Post a Mehrtens)—CaA'₂5aq S (of CaA'₂) 50 at 20° —SrA'₂5aq UAA'₂Daq S (OI CAA'₂) DU BY 20' — DIA 20A'₂ play yellow crystals (Marchand) S (Of CaA'₂) 14 at 20° — MgA'₂8aq S (Of MgA'₂) 10 at 22°.— MgA'₂8NaA' 9aq (Muller, Z 1865, 189) — CdA'₂7aq — CdA'₂5NH₃ (Carey Lea, Am S [2] 81, 78) — CdA'₂6NaA' 12aq — CuA'₂5aq green needles — CuA'₂5aq brown needles — CoA'₂4NH₃ — CoA'₂5aq brown needles — CoA'₂4NH₃ — CoA'₂5A₂ NA'₂5aq Saq NA'₂5aq Sag NA - CoA',5aq brown needles — CoA',4NH, — CoA',26NaA' 12aq — N1A',26NaA' 12aq — FeA',25aq yellow crystals — FeA',26NaA' 12aq — FeA',26NaA' 12aq — FeA',26NaA' 12aq — FeA',26NaA' 12aq — MnA',25aq (Muller) — MnA',25aq (Marchand) — PbA',2aq (E Kopp, A Ch [3] 13, 233) S 9 at 15° — PbA',2aq — PbA',0H) — Pb,A',2O,2 aq — Pb,A',2O,4 — Pb(OAc)A' 4aq — Hg,A',2 — AlA',2(OH) 8aq — ZnA',28aq S (of ZnA',2) 125 in the cold — ZnA',3NH,3 — ZnA',6NaA' 12aq — AgA' aq S 9 at 15° — AgA',2NH,3 Compounds of picric acid with organic bases and with aromatic hydro with organic bases and with aromatic hydro carbons, are described under those bases and hydrocarbons

Acetyl derivative CoH2(NO2)3OAc [76° Yellow crystals (Tomması a David, C R 77,

Benzoyl derivative C₆H₂(NO₂)₃OBz

Methylether MeA' Trinitroanisole [60°] (C), [64°] (Post a Mehrtens, B 8, 1552) Formed by nitrating PhOMe (Cahours, A 69, 238) and by methylation of pieric acid clinic tables (Friedlander, J 1879, 514)

Ethyl ether EtA' [78°] Long needles (Stenhouse a Muller, A 141,80, Willgeidt, B

12, 1277)

Iodoethyl ether C2H,IA' [70°]

the Ag salt and C.H.L. (Andrews, B 13, 244)

Phenyl ether PhA' Formed from KOPh
and C.H.CI(NO.), Needles (W)

o Nitro phenyl ether C,H,(NO,)A' [173°]

p-Nitro-phenyl ether C,H,(NO,)A' (155°) Plates (from alcohol) (Willgerodt, B 17, 1766)

Benzyl ether C.H.CH.A' [147°] Yellow

prisms (Kumpf, A 224, 131)

p-Nitro-benzyl ether C.H. (NO2) CH2A' [108°] Formed from silver picrate and p nitro-

benzyl 10dide (K)

(\$)-Tri-nitro-phenol C₆H₂(NO₂)₃OH[6 4 3 1] [96°] Formed, together with the (7) isomeride and tri nitro resorcin (styphnic acid) by the action of cone HNO₂ on (γ) di nitro phenol (Henriques, A 215, 325, of Bantlin, B 8, 21) Needles, v e sol alcohol and ether, m sol hot water Forms with naphthalene a compound [72°].—KA' violet needles, insol alcohol-BaA', 4aq red prisms

(γ)-Tri-nitro-phenol C₀H₂(NO₂)₂(OH)[6 3 2 1] [118°] Formed by nitrating (ε) dimitrophenol, and also, together with the (β) isomeride, by nitrating (γ)- or (δ) dimitrophenol (Henriques) White needles Readily converted into styphnic acid by boiling with fuming HNO, Forms with naphthalene a compound crystallising in yellow needles [100°] — KHA' red needles, insol alcohol —BaA'₂ · golden yellow scales.

References - Chloro, Bromo, and Iopo-NITRO PHENOL

o NITRO-PHENOL SULPHONIC ACID

 $C_bH_s(OH)(NO_2)(SO_3H)[1\ 2\ 4]$ [122°] Formed by sulphonating o nitro phenol (Kekulé, Z 1867, 641, Armstrong, Z 1871, 821, Armstrong a Brown, B 7, 923) Formed also by nitration of phenol p sulphonic acid (Schmitt a Glutz, B 2, 51, Körner, G 2, 444, Kolbe a Gauhe, A 147, 71) and by boiling (1, 2, 4) brome nitro benzene sulphonic acid (Goslich, A 180, 105) Needles (containing 3aq) Melts at 52° when hydrated, 122° when anhydrous -NH₄A' -NaA' 3aq -Na₂C₆H₂NSO₆ 3aq -KA' -K₂A'' aq -K₂A'' 2aq -BaA'₂ 2aq -BaA'₂ 2aq red crystals, sl sol

p Nitro-phenol sulphonic acid CoH, NSO, s.c. $C_i \hat{H}_s(OH)(NO_i)(SO_sH)[1 \ 4 \ 2]$ Formed from pnitro phenol and fuming H,SO, (Korner a Post, B 5, 852, 1055, 6, 395, 7, 163, A 205, 38) Formed also by nitrating phonol o sulphonic acid (Stuckenberg, A 205, 45) Crystals (con taining 3aq), beginning to decompose when heated at 110° Give a brown pp with FeCl₃— KA' monoclinic crystals, a b c = 1704 1 1 524, β=117° 59' — K₂A" aq — Na₄A' 2aq — Na₂A" 2aq — CaA'₂ 3aq — CaA'' 2 ½aq — BaA'₂aq — BaA'' aq — PbA'₂ 1½aq — CuA"

Nitro-phenol disulphonic acid $C_6H_5NS_2O_9$ i c C.H₂(OH)(NO₂)(SO₃H)₂ Formed from di nitro benzene disulphonic acid by reduction to nitro amido benzene disulphonic acid and displace ment of NH₂ by OH (Limpricht, B 8, 289) Minute needles —BaA" 2aq crystalline

D1-n1tro-phenol sulphonic acid $C_oH_4N_2SO_s \iota c$ C, H2(OH)(NO2) (SO3H) Formed by the action of nitrous acid on s di phenyl hydrazine disul phonic acid (Balentine, A 202, 358) Plisms from alcohol), v sol water Decomposes at 160°-KA' ½aq -K₂A'' 2aq -BaA'' 8½aq (Bertram, P Beibl 6, 779)

Tri-nitro-phenol sulphonic acid $C_0H(NO_2)_3(OH)(SO_3H)[6\ 4\ 2\ 1\ 3]$ Formed from phenol m sulphonic acid and HNO, (Beindsen, A 177, 92) -KA' aq prisms, exploding when heated -BaA' 23aq crystals, m sol water

o NITRO-DIPHENYL C_{1.}H₂NO, 1e C₂H₃C₃H₄NO₂[12] [37°] (c 320°) Formed, together with the p isomeride, by niti ition of diphenyl (Luddens, B 8, 870, Hubner, A 209, Thick plates (from 341, Schultz, A 207, 352) dilute alcohol)

p Nitro-diphenyl [113°] (340° 1 V) Formed as above (Schultz, A 174, 210, Hubner, Zimmermann, B 13, 1960) Long needles (from Yields p nitro benzoic acid on oxida tion

 ∞ D1-nitro-diphenyl C, H,N,O, ve [2 1]C,H,(NO₂) C,H,NO₂[1 2] [124°] from di nitro di p amido diphenyl by elimina tion of amidogen (Tauber, B 24, 197) yellow needles, sl sol cold alcohol

op Di-nttro-diphenyl C₁₂H₈N₂O₄ is [2 1]C₂H₄(NO₂) C₈H₄(NO₂)[1 4] [83 5°] Formed, together with the pp isomeride, by heating diphenyl with HNO₃ and H₂SO₄ (Fittig, A 124, 275, Schultz, Schmidt a Strasser, A 207, 349). Golden monoclinic needles, a b c = 108 1 91; B = 87° 30' More sol alcohol than the pp uso meride.

mm-Di-nitro diphenyl

[8 1] O₆H₄(NO₂) O₆H₄(NO₂) [1 8] [198°] Formed from di-hitro di p amido diphenyl by elimina-tion of the NH₂ groups (Brunner a Witt, B 20, 1028) Small yellow needles Yields di-mamido diphenyl on reduction

pp Di-nitro-diphenyl

[4 1]C₆H₄(NO₂) C₆H₄(NO₃)[1 4] [233°] (Schultz, A 174, 221) Formed as above Needles

Yields benzidine on reduction

Tetra-nitro-diphenyl C, H₆(NO₂), [140°]. Formed from diphenyl, H,SO,, and HNO, (Losanitsch, B 4, 404) Amorphous mass, al sol alcohol

O NITRO-PHENYL-ACETIC ACID C.H,NO. e C₀H₄(NO₂) CH CO H [138°] (B), [141°] Formed, in small quantity, in the prepa ration of the p isomeride by nitration of phenylacetic acid (Radziszewski, B 3, 548, Bedson, C J 37, 93) Obtained also by saponifying its nitrile (Gabriel a Borgmann, B 16, 2066) Needles (from water) or monoclinic plates (from Yields o nitro benzoic acid on oxida tion with KMnO, Gives oxindole on reduction —BaA', 2aq

Nitrile CoH, (NO2) CH, CN o Nitro benzyl cyanide [83°] (B), [84°] (S) Formed in small quantity, together with the m and p isomerides, by nitration of benzyl cyanide (H. Salkowski, B. 17, 507). Formed also, together with a larger quantity of the compound C₈H₄(NO₂) CHCy CH₂C₈H₄NO [111°] and small quantities of C15H2N3O3 [c 238°] and C2H14N4O4 [191°], by boiling o nitro benzyl chloride with alcoholic KCy (Bamberger, B 19, 2635) Tri

metric prisms

m-Nitro-phenyl-acetic acid [31]C₆H₄(NO) CH₂CO₂H [117°] (G & B), [120°] (S) Formed from the nitrile which is obtained from m nitro benzvl chloride and KCy Needles —AgA' silky needles
Nitrile [61°] Monoclinic crystals

p Nitro-phenyl-acetic acid [4 1]C₀H₄(NO₂) CH₂ CO₂H [152°] Formed as above (Radziszewski, B 2, 209, Maxwell, B 12, 1765, Gabriel, B 14, 2342, 15, 834, Bedson, C J 37, 92) Silky needles With o nitrophenyl acetic acid it forms a molecular compound [114°] Yields p oxy benzoic acid on oxidation Sodum amalgam yields N₂(C₂H₁CH₂CO₂H₂) [above 300°] (Wittenberg, Bl [2] 43, 111) — NaA' 2aq — BaA'₂ — BaA'₂ 7aq — ZnA'₂ aq — AgA' needles

[55°] Ne. Plates Methyl ether MeA' Needles Ethyl ether EtA' [65°] Plates
Amide [192°] Long prisms
Nitrile [116°] Plates Alcoholic KOH

forms a crimson solution in which diazobenzene chloride ppts $C_{14}H_{10}N_4O_2$ [202°] (Czumpelik, B 3, 474, Perkin, C J 43, 111)

D1-nitro-phenyl-acetic acid C₈H₆N₂O₆ t.e [4 2 1]C₈H₈(NO₂)₂CH₂CO₂H [160°] Formed from phenyl acetic acid, H_2SO_4 , and fuming HNO₃ (R , Gabriel a Meyer, B 14, 823) Formed also by boiling di nitro phenyl-aceto acetic ether with dilute H₂SO₄ (Heckmann, A 220, 128) Pale yellow needles, sol hot water Decomposed by heat into di-nitro toluene [71°] and CO.

Methyl ether MeA' Forms with diszobenzene chloride C,H,(NO,),C(N NHPh).CO,Me

[183°] (V Meyer, B 22, 319) Diazotoluene forms the homologous tolyl hydrazide of methyl di nitro phenyl glyoxylate [168°] crystallising in red needles (Hausknecht, B 22, 325) The corresponding derivatives of diazoxylene and di

azonaphthalene melt at 159° and 94° respectively Ethyl ether EtA' [55°] Needles When heated with alcoholic potash it yields $C_{2i}H_{18}N_{s}O_{18}$ [151°], which forms the salt $K_{2}C_{2i}H_{18}N_{s}O_{18}$, crys-

tallising in golden plates

Tetra-nitro-di-phenyl-acetic ether

{C_eH₇(NO)₂}₂CH CO₂Et [154°] Formed from sodium di nitro phenyl acetoacetic ether and biomo di nitro benzene (Von Richter, B 21, 2470) Crystalline — C₁₈H₁₁NaN₄O₁₀ [80°] very hygroscopic plates

p-NITRO-PHENYL-ACETIC ALDEHYDE

C₆H₄(NO₂) CH CHO [86°] Formed by boiling the barium salt of C₈H₄(NO₂) CHCl CH(OH) CO₂H with water (Lipp, B 19, 2645, cf Foirer, B 17, Needles, sl sol cold water

DI-NITRO-PHENYL-ACETOACETIC ETHER [4 2 1] C_bH₃(NO₂)₂ C 1Ac CO₂Et [94°] Formed from C, H, Br(NO2)2, acetoacetic ether, and NaOEt (Heckmann, A 220, 128) Plates

Tri-nitro-phe ivl-acetoacetic ether

C.H.(NO), CHAc CO.Et [98] Formed, together with {C.H.(NO)} CAC CO.Et [205°], from picryl chloride C.H.(Cl(NO₂), and sodium acetoacetic ether (Dittrich, B 23, 2720) Crystals, v sol hot alcohol

p-NITRO PHENYL ACETURIC ACID C₆H₄(NO₂) CH₂ CO NH CH₂ CO₂H [173°] Got by nitrating phenylaceturic acid (Hotter, J pr [2] 38, 110) Needles, decomposed by boiling HClAq into glycocoll and p nitro phenyl acetic acid — ZnA'_22 aq -AgA' needles, v sl sol cold water

o NITRO PHENYL ACETYLENE C,H,NO, te C,H,(NO,) C CH [82°] Formed by boiling o nitro phenyl propiolic acid with water (Baeyer, B 13, 2259) Needles, sol hot water Gives pps

with ammoniacal AgNO, and Cu, Cl2

p-Nitro phenyl acetylene [149°] (M), [152°] (D) Formed by boiling p nitro phenyl propiolic acid with water (Drewson, A 212, 158) Formed also from C,H,(NO2) CHBr CHBr CO2Et and alcoholic potash (C L Muller, A 212, 133) Needles (from hot water) Gives a red pp with ammoniacal Cu₂Cl₂ and a greenish yellow pp with ammoniacal AgNO,

D₁ p nitro d₁ phenyl-acetylene C₁₄H₈N₂O₄ t e C₆H₄(NO₂) C C C₆H₄NO₂ [288°] Formed from C₆H₄(NO₂) CHBr CHBr C₇H₄NO₂ by heating with soda lime at 180° (Elbs a Bauer, J pr [2] 34,

Yellow needles (by sublimation)

o Nitro di phenyl di acetylene C,6H,NO2 & 6. C₆H₄(NO₂) C C C CPh [155°] Formed by the action of K.FeCy, on a mixture of the cuprous salts of phenyl acetylene and o nitro phenylacetylene (Baeyer a Landsberg, B 15, 57). Yellow plates, sol alcohol

Di-o-nitro di phenyl diacetylene C_sH₄(NO₂) C C C C C_sH₄(NO₂) [212°] Formed by the action of an alkaline solution of K₃FeCy₆ on the cuprous salt of o nitro-phenyl acetylene (Baeyer, B 15, 51) Golden needles, sol chloroform Fuming H.SO, converts it into the isomeric dusatogen

NITRO-PHENYL-ACRYLIC ACID v. NITRO-CINNAMIC ACID

NITRO - DI - PHENYL - ACRYLIC ACID Netrale The o-, m-, and p-, varieties, melting at 128°, 134°, and 118° respectively, are formed by the action of the corresponding nitro-benzoic aldehydes on phenyl-acetic nitrile (benzyl cyanide) in presence of alcoholic NaOEt (Frost, A **250**, 160)

o-NITRO-PHENYL-ALLENYL-MALONIC ACID C.H.(NO.) CH CH CH C(CO.H). Formed by heating o nitro cinnamic aldehyde with malonic soid and HOAc at 100° (Einhorn, Needles -CuA".-Ag,A" A 253, 374)

lowish plates

p-Nitro-phenyl-allenyl-malonic acid [208°] Formed from p nitro-cinnamic aldehyde, malonic acid, and HOAc (Einhorn a Gehrenbeck, B 22, 45) Yellow needles (from HOAc) Br forms O.H. (NO2) CHBr CHBr CBr C(CO,H), [206°] crystallising in plates — (NH₄)₂A". –
CuA" — Ag₂A" floculent pp

Ethylether Et₂A" [105°] Needles

o-NITRO PHENYL-AMIDO ACETIC ACI

C₆H₄(NO₂) NH CH₂CO₂H [193°] Formed from bromo-acetic acid and o nitro aniline at 125° (Plöchl, B 19,6) Dark red prisms, sl sol ether Yields oxy-quinoxaline dihydride on reduction —

 $NH_{\bullet}A'$ flat orange prisms p - NITRO - PHENYL ω - AMIDO - ACETO PHENONE C₆H₃ CO CH₂ NH C₆H₄ NO₂ [167° Formed by heating its introsamine with HCl Mohlau, B 15, 2474) Golden needles (from Yields acetophenone and p phenylene-HOAc) diamine on reduction

Nitrosamine C_{1,H₁1}N₂O₄ is C₂H₃ CO CH₂ N(NO) C₃H₄ NO₂ Formed from phenyl-amido-acetophenone, HOAc, and nitrous Formed from acid gas (M) Plates, decomposing at 135°-145°

Di-nitro-phenyl ω-amido-acetophenone C_6H_3 CO CH_2 NH C_6H_3 (NO₂)₂. [172°] Formed by nitration of phenyl amido acetophenone (Möhlau, B 15, 2479) Golden prisms (from HOAc) Yields & tri amido benzene on reduction

s-TRI NITRO-TRI PHENYL TRI AMIDO BENZENE C₆(NHPh)₃(NO₂), [238°] Formed from C₈Br₄(NO₂), and annline (Jackson a Wing, Am 10, 283) Orange powder, insol water

m - NITRO - PHENYL - p AMIDO - BENZOIC ACID C₆H₃(NO₂)(NHPh) CO₂H[3 4 1] Formed by heating (4,3,1) bromo nitro benzoic acid with aniline (Schöpff, B 22, 3281) Garnet red needles Yields an amido- acid [153°] -NaA' — NaA'aq — BaA'₂ 3aq — AgA' plates

Ethyl ether EtA' [123°] Hexagon Anrilede CeH. (NO2) (NHPh) CONHPh [123°] Hexagonal [216°] Formed by heating aniline with bromo nitro-benzoyl chloride (Grohmann, B 23, 3448) Blood red leaflets from HOAc

Natrals C_eH_s(NH₂)(NHPh) CN Formed from bromo nitro benzonitrile and ani

me (Schöpff, B 23, 3444)

o-Nitro-phenyl-m amido-benzoic acid C₆H₃(NO₂)(NHPh) CO₂H[2 3 1] [248°] Formed from (3,2,1)-bromo-nitro-benzoic acid and am-line (Schöpfi, B 23, 8440) Yellow needles — NaA'2aq —BaA',5aq

Ethyl ether EtA' [112°] Needles m-Nitro-phenyl-o-amido-benzoic acid Nitrile C_eH₂(NO₂)(NHPh)CN[5 2 1] [170°] Formed from (2,5,1)-bromo-nitro-benzonitrile and aniline (S.) Lemon-yellow needles

Di-nitro phenyl-o-amido-benzoic acid C₁₈H₄N₃O₆ * c [4 2 1]O₆H₂(NO₂)₂ NH C₃H₄ CO₂H₄.

[264°] Formed by warming c amid benzone acid with C₆H₄Cl(NO₂)₂ (Jourdan, B 18, 1448)

Orange needles, almost insol. water—BaA'₂ dark red crystalline powder

NITRO-PHENYL-AMIDO-NAPHTHOQUIN. ONE v (a)-Napthoquinone, Reactions 16 and

DI-NITRO-PHENYL-DI-AMIDO-DIPHENYL C₁₈H₁₄N₄O₄ te C₆H₄(NH₂) C₆H₄ NH C₆H₅(NO₂)₂
[245°] Formed by boiling benzidine with alco hol and (1,2,4) chloro di nitro-benzene (Will-gerodt, B 9, 981) Long needles (from HOAc) Di o nitro-di-phenyl diamido diphenyl

C₆H₄(NO₂) NH C₆H₄ C₆H₄ NH C₆H₄(NO₂) [240°]. Formed by boiling benzidine with o chloro nitrobenzene and alcohol (Schöpff, B 22, 904)

Needles (from HOAc)

Tetra nitro di phenyl di amido diphenyl C₆H₃(NO₂)₂NH C₆H₄ C₅H₄ NH C₆H₃(NO₂)₂ [above 330°] Formed from [1 2 4]C₅H₅Cl(NO₂), alcohol, and benzidine at 120° (W) powder, sl sol alcohol

DI NITRO PHENYL AMIDO-TOLYL AMINE [4 2 1]C₆H₃(NO_{.)2}NH C₆H₃Me NH₂ [147°] Formed from tolylene o diamine and a chloro di nitro benzene (Ernst, B 23, 3428) Brownish yellow needles Yields with HNO₂ the azimide

 $C_eH_a(NO_2)_zN < {C_7H_6 \atop N} N$ [186°]

o nitro di phenyl amine $C_{12}H_{10}N_2O_2\imath$ s [2 1]C_bH₄(NO₂) NHC_bH₄, [75°] Formed from aniline and o chloro nitro benzene or o bromo nitro benzene at 100° (Schopff, B 22, 903, 23, 1839) Trimetric crystals (from alcohol), abc = 4681 671Yields on reduction the amido compound [80°]

v Nitro-diphenylamine $[4\ 1]C_6H_4(NO_2)$ NH C_6H_5 [133°] Formed from benzoyl diphenylamine by nitration and elimi nation of Bz (Hofmann, A 132, 167, Lellmann, B 15, 825) Formed also from its nitrogamine by treatment with aniline (Witt, C J 33, 205) Pale-yellow scales (from dilute alcohol) Colours alcoholic potash scarlet Dyes silk yellow

Benzoyl derivative [129°] Prisms CaH, (NO2) N(NO) CaH, Nitrosamine [134°] Formed by warming diphenylamine with HNO, isoamyl nitrite, and alcohol (W) Crystals, sol chloroform

Di-o-nitro diphenylamine NH(C,H,NO), Obtained from its [220°] (L), [212°] (W) benzoyl derivative, and also, together with the p-isomeride, by the action of alcohol (50 cc), aniline (25 g) and aniline hydrochloride (30 g) at 100° on the mixed di nitro di phenyl nitros amines prepared from diphenylamine (17 g), amyl nitrite (48 g), alcohol (50 c c), nitric acid (40 cc of SG 1424), and HOAc (50 cc) (Witt, C J 33, 208) Red felted needles

NBz(C,H,NO,), Benzoyl derivativeFormed, together with that of the p isomeride from benzoyl diphenylamine and fuming HNO. (Lellmann, $B \,\,$ 15, 827)

Di p-nitro-diphenylamine $C_{12}H_1N_2O_4$ is $NH(C_4H_4NO_2[1\ 4])_2$, $[216^\circ]$ (L), $[214^\circ]$ (W) Got as above Yellow needles with blue reflex Bensoyl derivative [224°] Monoclinie

crystals, sl sol alcohol.

Di nitre diphenylamine $C_{12}H_1N_1O_4$ s.e C_2H_1 NH C_1H_2 (NO₂)₂ or C_2H_2 (NO₂)₂ and annine or d_1 phenyl thie urea (Clemm, B 3, 128, Willgeredt, B 9, 977, 11, 601, of Hepp, Bl [2]

Tri-nitro diphenylamine C₁₂H₆N₄O₆ 1 6 I₅ NH C₆H₂(NO₂)₆[1 2 4 6] [175°]. I C₆H₅ NH C₆H₂(NO₂)₃[1 2 4 6] Formed from $C_{\bullet}H_{\bullet}Cl(NO_{s})_{\bullet}$ (picryl chloride) and aniline (Clemm, B 3, 126) Scarlet prisms Scarlet prisms

Trı nitro diphenylamine

3 1]C₆H₄(NO₂) NH C₆H₃(NO₂)₂[1 2 4] [194°] Formed from C₆H₃Br(NO₃)₂ or C₆H₃Cl(NO₂)₂ and m nitro annine (Austen, B 7, 1250, Willigerodt, B 9, 1178) Short yellow needles (from HOAc) Tri nitro-diphenylamine

[4 1] $C_8H_4(NO_2)$ NH $C_8H_4(NO_2)_x$ [181°] Formed from p nitro aniline and bromo di nitro benzene

Yellow powder, v e sol HOAc

Tri nitro diphenylamine [135°] by boiling the acetyl derivative of diphenylamine with dilute nitric acid (SG 1029) (Norton a Allen, B 18, 1997) Yellow needles, v sol alcohol

C12H,N,O Tetra nitro diphenylamine [205°] $[3\ 1]C_4H_4(NO_1)$ NH $C_4H_2(NO_2)_2[1\ 2\ 4\ 6]$ Formed from m nitro aniline and picryl chloride (Austen, B 7, 1248) Orange crystals (from HOAc)

Tetra nitro diphenylamine

 $[4\ 1]C_6H_4(NO_2)$ NH $C_6H_2(NO_2)_2[1\ 2\ 4\ 6]$ [216°]. Formed in like manner from p-nitro aniline (A)

Tetra nitro diphenylamine NH{C,H,(NO,),2}.
[180°] Got by heating C,H,(NO,),2 NH CO,Et with alcoholic potash (Hager, B 17, 2629) Reddish brown plates (from alcohol)

Tetra nitro diphenylamine [192°] Formed by nitration of diphenylamine, diphenyl nitros amine, and diphenyl methylamine NMePh (Gnehm a Wyss, B 10, 1318) Yellow crystals (from alcohol) Forms a scarlet solution in

NaOH Aq

Hexa nitro-diphenylamine $\{C_6N_2(NO_2)_3\}_2NH$ Dipicrylamine [238°] (A), [234°] (M) Formed by nitrating diphenylamine, diphenyl methylamine, or tetra nitro diphenylamine [216°] (Austen, B 7, 1250, Gnehm, B 7, 1399, 9, 1245, 1557, Mertens, B 11, 845) Yellow prisms acetic acid) Its ammonium salt NH₁C₁₂H₄N₁O_{1,2} is used as a yellow dye ('auranita') —Ba(C₁, H₁N₁O_{1,2}) red rhombohedra

Hexa nitro diphenylamine [261°] Formed

by nitrating tetra nitro diphenylamine [205°] (A) Small yellow crystals (from HOAc). Ex-

plodes when heated.

Nitro tri phenyl amine (C,H,)2N C,H,(NO2) Formed from triphenylamine, HOAc, and HNO, (Herz, B 23, 2537) Golden plates

Di nitro-tri phenyl amine CoH,N(CoH,NO2)2 Formed from triphenylamine HOAc (35 g) and HNO, (2 g) at 60° (Herz, B 23, 2538) Yellow needles, v sol benzene

Tri nitro-tri-phenylamıne N(C,H,NO,), [280°] Formed from triphenylamine (2g), HOAc (35g), and HNO, (4g) at 100° (Heydrich, B 18, 2156; Herz, B 23, 2539). Bronze-yellow needles, v sl sol. HOAc

m NITRO-PHENYL-ANGELIC ALDEHYDE O.H.(NO.) OH CEt OHO [46°] Formed from m nitro benzoio aldehyde, butyric acid, and dilute NaOHAq (Von Miller a. Rohde, B. 22,

1838) Plates, reduced by tin and HCl to

amido-ethyl indonaphthene [89°]

Phenyl hydrasids [135°] Red i

DI NITRO DI-p-PHENYL BENZENE Red needles. $C_{18}H_{12}(NO_2)_2$. [277°] Formed by nitration of diphenylbenzene (Schmidt a Schultz, B 11, 1755, A 203, 125) Yellow monoclinic needles (from nitro benzene)

Tri-nitro-di-p-phenyl-benzene C18H11(NO2)3 [195°] Formed from diphenylbenzene and fuming HNO, (S a S) Needles Yields on

reduction a base [170°]

Tri-nitro diphenylbenzene [200°] Formed by nitration of isodiphenylbenzene (S a S). Needles Yields on reduction a base [288°]

Tetra-nitro-tri-phenyl-benzene C24H14(NO2)4 [above 370°] Formed, together with an isomeride [108°], by nitrating triphenylbenzene (Mel lin, B 23, 2535) Both bodies crystallise in needles

NITRO-PHENYL-BENZYLIDENE-AMINE $C_{13}H_{10}N_2O_2$ to C_6H , CH N C_6H , NO_2 . [66°] (Lazorenko, J 1870, 760), [73°] (Lachovitch, M 9, 695) Formed from benzoic aldehyde (or hydrobenzamide) and m-nitro aniline Needles

p Nitro phenyl-benzylidene-amine C,H, N C,H, (NO2) [1 4] [115°] Formed from hydrobenzamide by warming with p nitro-aniline Yellow needles (Lachovitch)

Isomerides v Nitro benzylidene anilite NITRO-PHENYL BENZYL OXIDE

C₆H₄(NO₂) O CH₂Ph Formed from potassium nitro phenol, alcohol, and benzyl chloride (Kumpt, A 224, 121) The o-compound melts at 29°, and the p compound at 106° Both are crystalline

Di nitro phenyl benzyl oxide C18H10N2O, i e C₆H₃(NO₂)₂ O CH₂Ph Formed from silver di nitrophenol and benzyl iodide (K) The (4,2,1)compound melts at 149°, and the (6,2,1) com pound at 76° (OH=1) Both crystallise from HOAc

Tri nitro phenyl bensyl oxide C₁₃H₈N₂O₇ s.e [6 4 2 1] C₆H₂(NO₂)₃ O CH₂Ph [147°] Formed from silver picrate and benzyl iodide (K.). lellowish prisms (from benzene)

TRI-NITRO - DI - PHENYL - BENZYL-PHOS-PHINE OXIDE PO(C₆H₄NO₂)₂(C₇H₈NO₂) [206°]₄ Formed from the oxide, fuming HNO, and cone H₂SO₄ (Dorken, B 21, 1505) Crystals, m sol HOAc

DI-NITRO-PHENYL-BENZYL SULPHIDE C,H, S C,H,(NO,), [1 2 4] [128°] from (1,2,4) chloro di nitro-benzene, Formed alcoholic K2S, and benzyl chloride (Willgerodt, B 18, 331) Yellowish plates

NITRO-PHENYL-BROMO-PROPIONIC ACID . BROMO-VITRO PHENYL PROPIONIC ACID

o - NITRO - PHENYL - BUTINYL METHYL ERTONE C.H.(NO.) C.H. CO CH. [78 5°]. Formed, together with (C.H.(NO.) C.H.).CO [208 5°], from o nitro cinnamical dehyde, acetone, alcohol, and dilute (2 pc) NaOHAq (Diehl a. Einhorn, B 18, 2327) Broad needles (from

o-NITRO-PHENYL-BUTINYL PHENYL-BUTINYL KETONE C.H., NO. s.c. C.H.(NO.) C.H. CO C.H. C.H. [136 5°]. Formed from o nitro-cunnamic aldehyde, phenyl-butinyl methyl ketone, alcohol, and dilute NaOHAq

(Diehl a Einhorn, B 18, 2829) Golden crystals (from acetone)

p-NITRO-PHENYL-ISOBUTYRIC ACID C₆H₄(NO₂) CH₂ CHMe CO₂H [121°] Formed from phenyl isobutyric acid and cone HNO₃ (Edeleanu, C. J 53, 559) Small prisms, sol

alcohol

NITRO-PHENYL-CARBAMIC ETHER

CeH4(NO2) NHCO2Et The o compound [58°] and the p compound [129°] are got from the corre sponding nitro aniline and ClCO, Et (Rudolph, \bar{B} 12, 1295, Hager, B 17, 2625) The p compound is also got by nitration of phenyl car-bamic ether (Behrend, A 233, 9) Both are crystalline

Di nitro-phenyl carbamic ether C₈H₉N₃O₆ i e [4 2 1] C₆H₄(NO₂)₂NH CO₂Et [111°] Formed by nitration of either o- or p nitro phenylcanbamic ether (Hager, B 17, 2629) Needles (from alcohol) An isomeride [210°] is got by the action of HNO, on C, H, NH CS OEt (Losa-

nitsch, B 10, 691)

Di nitro di phenyl carbamic ether

(C₆H, NO₂)₂N CO₂Et The only o- compound is formed together with the p-compound [134°] by nitration of di phenyl carbamic ether (Hager, B 18, 2574) The p-compound is the less sol. alcohol

m-NITRO-TRI-PHENYL-CARBINOL

C,H,(NO2) CPh2 OH Formed from [75°] C.H.(NO.) CHPh2 by bromination in sunlight, followed by successive treatment with KOAc and KOH (Tschacher, B 21, 190) Colourless crystals, sol ligroin

p Nitro-tri phenyl-carbinol [136°] Formed by oxidising p nitro tri phenyl methane with CrO, in HOAc (Baeyer a Lohr, B 23, 1623)

Crystals (from dilute HOAc)

Tri-p-nitro tri phenyl carbinol C₁₀H₁₁N₃O, te (O₆H₄NO₂)₃COH [172°] Formed by oxidising tri nitro tri-phenyl methane (E a O Fischer, B 11, 1079) Colourless crystals (from HOAc)

TETRA-NITRO-DI-PHENYL CARBONATE $(C_0H_s(NO_2)_2)$,CO [127°] Formed from di phenyl carbonate, HNO_s, and H,SO_s (Kempf, J pr [2] 1, 407, Löwenberg, C C 1886, 390) Nodules, w sl sol ether

NITRO - DIPHENYL CARBOXYLIC ACID C₁₃H₂(NO₂)O₂ [222°] Formed by nitration of diphenyl o carboxylic acid (Schmidt, A 193, 115) BaA', Monoclinic crystals (from alcohol) --CaA'2 nodules, v sol water

Nitro diphenyl carboxylic acid C14HeNOe i e $[2\ 1]\ C_6H_4(CO_2H)\ C_6H_3(NO_2)\ CO_2H\ [1\ 4\ 2]\ [217^\circ]$ Formed by oxidation of nitro phenanthraquinone [257°] (Strasburger, B 16, 2347) Light yellow needles (from water)

Di nitro-diphenyl carboxylic acid

 $[4\ 1]\ C_6H_4(NO_2)\ C_6H_3(NO_2)\ CO_2H\ [1\ 2\ 4]\ [252^\circ]$ Formed by nitrating diphenyl p carboxylic acid (Strasser a Schultz, A 210, 192) Needles, m sol alcohol

Methyl ether MeA' [156°] Needles (a)-Di nitro diphenyl dicarboxylic acid

 $C_{12}H_6(NO_2)_2(CO_2H)_2$ [249°] (H), [253°] (Schultz, A 196, 26) Formed by oxidation of di nitro phenanthraquinone (Struve, B 10, 75), and, together with the following acid, by nitration of diphenyl dio carboxylic acid (Hummel, A 193, 129) Pale yellow needles (containing aq) -BaA' 6ag long prisms.

Methyl ether Me, A". [178°] Prisms.
(β) - Di - nitro - diphenyl dicarboxylic acid.
[297°] Formed as above (Schultz, A 203, 105). Needles (from hot water) -BaA'2 4aq triclinic prisms

Methyl ether Me,A" [132°] Tables NITRO - PHENYL CHLORO - METHYL KE TONE v CHLORO NITRO ACETOPHENONE

o NITRO-PHENYL CINNAMIC ACID

H₁₁NO₄ [196°] Formed from o nitro benzoic aldehyde, sodium phenyl acetate, and Ac,O at 160° (Oglialoro a Rosini, G 20, 396) Needles

-BaA" 5aq -BaA" 8aq NITRO-PHENYLENE o DIAMINE

 $C_6H_3(NO_2)(NH_2)_2$ [4 2 1] $[198^{\circ}]$ Formed by reducing (4,2,1) di nitro aniline with alcoholic ammonium sulphide (Gottlieb, A 85, 27, Heim, B 21, 2805) Dark red plates (from toluene).

Ac.O at 190° forms C₆H₄(NO₂) N₁H CMe [216°].

-B'HCl aq -B'₂H₂PtCl₈ -B'HNO₃ -B'₂H₂SO₄

-B'₂H₂C₂O₄ -B'₂H₂PtCy₄5aq

Dracetyl derivative [227°] Needles

Nitro phenylene m diamine C.H., N.O. 1 e $C_bH_s(NO_s)(NH_2)_2$ [161°] Obtained from its diacetyl derivative, which is got by nitrating $C_bH_s(NHAc)_2$ (Barbaglia, B 7, 1259) Yellowish red prisms, sol water

Di acetyl derivative C, H, (NO2) (NHAc)2

[246°] Slender needles (from alcohol)

Di benzoyl derivative Got by nitrating $C_6H_3(NO_2)(NHBz)_2$ [222°] dibenzoyl phenylene m diamine (Ruhemann, B 14, 2652) Needles (from HOAc)

Nitro phenylene p diamine $C_sH_s(NO_s)(NH_s)_2[2\ 4\ 1]$ [137°] Formed from its diacetyl or dibenzoyl derivatives, got by nitra ting the corresponding derivatives of phenylene p diamine (Ladenburg, B 17, 149, Hinsberg, A254, 255) Dark needles with green lustic

Di acetyl derivative C.H. (NO2) (NHAc)2 [186°] On warming with NaOHAq it yields the mono acetyl derivative crystallising in red

needles [195°

Di nitro phenylene diamine C₆H₆N₄O₄ i e $C_sH_2(NO_1)_2(NH_2)_2$ [211°] Formed by reducing picramide $C_sH_2(NO_2)_3NH_2$ [6 4 2 1] with aimmo nium sulphide (Norton a Elliott, B 11, 327) Red needles, almost insol cold water

Dr acetyl derivative C6H2(NO2)2(NHAc)2

[246°] Yellow needles

Di-nitro-phenylene-m diamine

 $C_6H_2(NO_2)_2(NH_2)_2[4\ 2\ 3\ 1]$ [c 250°] Formed by heating di nitro resorcin with aqueous am monia (Barr, B 21, 1545) Brownish needles (from HOAc), sl sol alcohol

Di nitro-phenylene-m-diamine

C₈H₂(NO₂)₂(NH₂)₂ [c 300°] Obtained by saponincation of its di acetyl derivative which is formed by nitration of di acetyl m phenylenediamine (Nietzki a Hagenbach, B 20, 333). Orange yellow crystals

Di acetyl derivative [228°] Needles Di nitro-phenylene-p diamine Di acetyl derivative [258°] Formed by nitrating di-

acetyl phenylene p diamine (Nietzki a Hagenbach, B 20, 331) Yellow solid, sl sol alcohol Tri-nitro-phenylene m diamine C.H.N.O., te C.H.NO.J. (NH.). [6 4 2 3 1] [above 250°]. Formed by boiling the di ethyl ether of tri-nitro resorcin with alcoholic ammonia (Nölting a. Collin, B 17, 260, Barr, B. 21, 1546).

Yellow granules Reduced by SnCl, and HCl to unstable penta amido benzene NITRO-DIPHENYLENE-KETONE C₁₈H₇NO₈

i.e , $\begin{bmatrix} 3 & 6 \\ 1 \end{bmatrix}$ C_6H_1 (NO₂) $< \begin{matrix} C_6H_4 \\ CO \end{matrix}> \begin{bmatrix} 220^\circ \end{bmatrix}$ Formed, as well as di nitro diphenylene ketone [290°], by nitration of o diphenylene ketone (Schultz, A 203, 103) The isomeric nitro derivative of iso diphenylene ketone [83°] melts at 220°-230° (Carnelley a Dunn, B 21, 2005)

Nitro-diphenylene-ketone carboxylic acid [246°] Got by warming di $\mathbf{C}_{14}\mathbf{H}_7(\mathrm{NO}_2)\mathbf{O}_3$ phenylene ketone carboxylic acid with HNO, (Fittig a Liepmann, A 200, 6) Golden needles (from alcohol) -BaA'2 4aq yellow needles, sl sol water

(a) - DI NITRO DIPHENYLENE KETONE

OXIDE C₆H₃(NO₂)<0>C₆H₃(NO₂) [190°] Formed, together with a (β) isomeride [260°]. warming diphenylene ketone oxide with HNO, (Wichelhaus a Salzmann, B 10, 1401, R Richter, J pr [2] 28, 292, A G Perkin, C J 43, 189, Gracbe, A 254, 286) An iso

meric body [224°] is formed, together with a di nitro-derivative [235°], by nitration of iso di phenylene ketone oxide [91°] (R) NITRO - PHENYLENE - DI - METHYL-O DI

AMINE $C_6H_3(NO_2)(NMe_2)(NH_2)[4 1 2]$ Formed by reducing di nitro dimethylaniline by ammonium sulphide (Heim, B 21, 2308) Orange needles (from water)

Nitro-phenylene tri methyl diamine

 $C_6H_3(NO_2)(NMe_2)(NHMe)$

Acetyl derivative [c 210°]

Netrosamene C,H,(NO2)(NMe2)(NMeNO) [87°] Formed from C,H,(NMe,), and HNO in excess (Wurster a Schobig, B 12, 1811) Needles

Tri nitro phenylene di methyl diamine O₈H₉N₃O₆ ie C₆H(NO)₃(NHMe), [235] Formed by heating its nitramine with phenol or aqueous methylamine (Romburgh, R T C 7,6,

8, 279) Golden crystals (from HOAc)

Di nitramine C₈H(NO₂),(NMe NO₂)

Formed by boiling C₈H₁(NMe₂), with fuming HNO₄ (Romburgh, R T C 6, 252) Pale yellow crystals, decomposing at about 205° nitramine C₆H(NO)₃(NHMe)(NMeNO₂) is got by the action of methylamine on C₆H(NO₂), NMeNO It separates from HOAc in golden crystals [192°]

NITRO-PHENYLENE (a) NAPHTHYL o DIAMINE C₆H₃(NO)(NH₂)(NHC₁₀H₇) Formed from (4, 2, 1) di nitro phenyl (a) naph thylamine and ammonium sulplide (Heim, B 21, 2302) Needles (from HOAc), v e sol alco The isomeric compound from di nitrohol phenyl (3) naphthylamine melts at 195°, and yields an acetyl derivative [200°], which is con verted by Ac₂O into nitro phenylene (β) naph thyl acetamidine (162°

DI-NITRO-PHENÝLENE NAPHTHYLENE OXIDE C₁₆H₈(NO₂)₂O [235°] Formed by nitrating (a) phenylene (a) naphthylene oxide (Arx, A 209, 141) V sol ether and HOAc

NITRO-PHENYLENE NAPHTHYL-ACET-AMIDINE $C_0H_3(NO_2) < N(C_{10}H_7)$

Formed from nitro amido phenyl (8) naphthylamine and Ac₂O (Heim, B 21, 589) Needles. DI-NITRO-DIPHENYLENE OXIDE

C₁₂H₄(NO₂)₂O. [200°] Formed from diphenyl-

ene oxide and fuming HNO, (Hoffmeister, A. 159, 211) Crystals (from alcohol)

NITRO PHENYLÈNE-UREA C,H,N,O, 1.4. C₆H₅(NO₂)<NH>CO Formed by heating nitro amido phenyl carbamic ether (Hager, B 17,

Colourless needles, not melted at 300°. NITRO-u DI-PHENYL ETHANE

C₄H₄(NO₂) CHPh CH₂ [80°] Formed, together with (C₄H₄ NO₂)₂CH CH₃ [149°], by nitration of u di phenyl ethane (Anschütz a Romig, B 18, Long yellow needles

 \mathbf{D}_{1-p} nitro-s di phenyl ethane [4 1] $C_6H_4(NO_2)$ CH_2 CH_2 $C_6H_4(NO_2)$ [1 4] [179°] Formed, together with an isomeride [75°], from dibenzyl and fuming HNO, (Stelling a Fittig, A 137, 260, Leppert, B 9, 15) Formed also from

p nitro benzyl chlorde, SnCl₂, and NaOHAq (W Roser, A 238, 364) Needles, sl sol alcohol. DI NITRO DI PHENYL ETHANE DICARB OXYLIC ACID C16H12(NO2)2O4 Formed by ni trating s di phenyl ethane di o carboxylic acid (Dobreff, A 239, 70) Minute crystals, melting above 300° — CaA"

Ethyl ether LtHA"

Di nitro di phenyl ethane dicarboxylic acid Formed by nitration of s di phenyl ethane as dicarboxylic acid (Reimer, B 14, Amorphous (containing aq) 1802) An 180 meric acid [242°] is got by nitrating s di phenyl ethane aa dicarboxylic acid Both acids yield p nitro benzoic acid on oxidation

CARBONATE o NITRO PHENYL-ETHYL C₆H₄(NO₂) OCO OEt (275° 285°) Formed by the action of chloro formic ether upon the potas sium salt of o nitro phenol (Bender, B 19, 2268)

Heavy vellow oil

NITRO-PHENYL-ETHYLENE NITEO-STYRESH

Nitro s di phenyl ethylene

C.H.(NO₂) CPh CH₂ [86°] Formed from C.H.(NO₂) CPh(OH) CH, and AcCl (Anschutz a Formed from Romig, B 18, 664) Yellow crystals (from ether) Di-o nitro di phenyl ethylene

(C_oH₄(NO)) C_iH Formed in two modifications 'cis' [126°] and 'trans' [196°], by the action of alcoholic potash upon o nitio benzyl chloride (Bischoff, B 21, 2072, 23, 2072) Both crys. tallise in needles

Di p nitro di phenyl ethylene Formed in two modifications, [e 213°] and [c 282°], by the action of alcoholic potash on p intro benzyl chloride (Walden, B 23, 1959, cf Strakosch, B 6, 328) Both are crystalline 6, 328)

DI - m - NITRO-DI - PHENYL - ETHYLENE -**DIAMINE** $(C_6H_4(NO_2) NH)_2C_2H_4$ [206°] Ob tained by heating m nitro aniline with ethylene bromide at 130° (Gattermann a Hager, B 17, Reddish yellow crystals, insol alcohol NITRO s-DI-PHENYL-ETHYLENE CAR

CARB. OXYLIC ACID Netrele C_sH₄(NO₂) CCy CHPh [176°] Got from p-nitro-phenyl acetonitrile, benzoic aldehyde, and alcoholic NaOEt at 50° (Remse, B 23, 3134). Yellow needles By using o or m nitro benzoicaldehyde, the corresponding di nitro-compounds [4 1] C₆H₄(NO₂) CCy CH C₆H₄(NO₂) [2 1] [185°] and [4 1] C₆H₄(NO₂) CCy CH C₆H₄(NO₂) [3 1] [195°] may be made Both crystallise in needles.

***MITRO-PHENYL-ETHYLENE-QUINOL-

INE CANHACH CH CAHANOA [136°] tained by heating methyl quinoline (lepidine) with m nitro benzoic aldehyde and KHSO, at 160° (Heymann a Königs, B 21, 1424). Needles

NITRO-PHENYL ETHYL KETONE

C₆H₄(NO₂) CO₂C₂H₅ [100°] Formed, together with a syrupy isomeride, by nitration of phenyl ethyl ketone (Barry, B 6, 1007) Prisms

NITRO.PHENYL.FURFURYL.ACRYLIC ACID Netrele C₆H₄(NO₂) CCy CH C₄H₂O [173°] Formed from furfuraldehyde, p nitro phenyl acetonitrile, and alcoholic (Freund a Immerwahr, B 23, 2852) Needles

o-NITRO-PHENYL-GLYCIDIC ACID C₅H₇NO₅ aq 1 e C₆H₄(NO₂) C₂H₂O CO₂H Nitro phenyl oxyacrylic acid [108⁵] Formed from C,H,(NO,) CH(OH) CHCl CO,H and alcoholic potash (Baeyer, B 13, 2262, Morgan, B 17, 219, Lipp, B 19, 2649) Prisms (containing aq) Melts at 94° when hydrated, 108° when anhydrous Yields indigo and CO2 on heating -NH₄A' aq —AgA' white crystalline pp

p-Nitro-phenyl-glycidic acid Formed in the same way as the o isomeride (Lipp), and also by the action of HOCl on so dium p nitro cinnamate (Erlenmeyer, B 14, 1868) Plates (from hot water) C₀H₄(NO₂) CH(OH) CH(OH) CO₂H on Yields boiling with dilute H.SO.

NITRO-PHENYL GLYCOCOLL Nitro PHENYL AMIDO ACETIC ACID

NITRO-PHENYL GLYCOLLIC ACID v GLY-COLLIC ACTI

o-NITRO PHENYL GLYOXYLIC ACID

C₆H₄(NO₂) CO CO₂H [49°] Formed from its amide, which is got by the action of cold cone HClAq on C₄H₄(NO₂) CH₂Cy (Clausen a Shad well, B 12, 352, Fehrlin, B 23, 1577) Needles A mide [189°] (C a S), [199°] (F)

Nttrile [54°] Prisms (from ligroin)

Phenyl hydrazide [166°] Changed by dissolving in alcoholic KOH and adding HCl into an isomeride [190°] HNO, converts the first phenyl hydrazide into a body melting at 77°-80°, and the second into one melting at 95°-100° Both yield isatin phenyl hydrazide on reduction The ethyl ether of the phenylhydrazide C₁₆H₁₅N₄O₃ crystallises in yellow prisms [128°] (Krause, B, 23, 3617)

Phenyl-methyl hydrazide [142°]

Oxim of the ethyl ether C,H,(NO2) C(NOH) CO2Et C₈H₄(NO₂) C(NOH) CO₂Et [163°] I (from boiling water) (Gabriel, B 16, 519) Needles

m-Nitro-phenyl glyoxylic acid [78°] Formed by boiling its amide with alkalis (Claisen a Thompson, B 12, 1944, 14, 1187

KA' flat prisms —BaA'2 aq —AgA'

A mide CaH4(NO) CO CONH2. Prisms nodules

[152°] Formed from m nitro phenyl acetonitrile, and also by nitration of phenyl-glyoxylic amide

Nitrile (231° at 145 mm) Oil
Phenyl hydraside [176°] (F) Crystals
Successive treatment with KOH and HClAq yields a green compound [285°]

Di-nitro-phenyl-glyoxylic acid Phenyl-hydrazide of the methyl ether C.H.(NO.). C(N.HPh) CO.Me [183] Formed Formed from methyl-di-mitro-phenyl-acetate and diazo-benzene chloride (V. Meyer, B 22, 319) Alcoholic potash forms a blue solution, changing to

yellow, and forming C_sH_s(NC_s)<\frac{C(CO,H)}{NPh N} [272°], which yields a methyl ether [132°]

m NITRO-DIPHENYL-GUANIDINE NH C(NHPh) NHC₆H₄NO₂. [132°]. Formed from m nitro di-phenyl thio urea, PbO, and al Formed coholic NH₂ (Brickner, B 7, 1236) Cyanogen, followed by dilute HClAq, changes it to the oxalyl derivative [168°], whence hot conc HCl forms nitro di phenyl parabanic acid (Hirsch, C C 1888, 624)

m-Nitro-tri-phonyl-guanidine Formed from m nitro-di phenyl thio urea, PbO, and aniline (B, Losanitsch, B 16,50) Yellow plates -B',H,PtCl,

m Di-nitro di phenyl-guanidine NH C(NH C,H,NO₂). [190°] Formed from m nitro aniline and cyanogen chloride (Hof Formed from mann, A 67, 156), or from di nitro di phènyl thio urea, PbO, and alcoholic NH₂ (B) Scales B'HCl -B',H,PtCl,

Tri m nitro tri phenyl guanidine C.H.(NO₂) N C(NH C.H. NO₂)₂. [189°] Formed from di nitro di phenyl thio urea, nodine, and alcohol (L) Yellow plates, sol hot alcohol

DI-NITRO DI-PHENYL HEPTANE $C_7H_{14}(C_6H_4NO_2)_2$ Oil (Auger, Bl [2] 47, 42) o NITRO PHENYL-HYDRAZINE

C₆H₄(NO₂)NH NH₂ [90°] Formed from onitro diazobenzene chloride, HCl, and SnCl, at 0° (Bischler, B 22, 240, 2801) Brick red needles from benzene), sl sol cold alcohol With benz oic aldehyde it yields C₆H₅CH N NH C₆H₁NO₂ [187°]—B'HSnCl₂ prisms—B'HCl needles—B'₂H₂SO₄ flesh-coloured needles

Formyl derivative C.H.(NO.) NH NHCHO [177°] Formed from o nitro phenyl hydrazine hydrochloride, formic acid, and some Na₂CO₃ Needles, v e sol hot Aq

Acetyl derivative [141°] Needles Di-acetyl derivative [58°] Prisms Bensoyl derivative [166°]
Oxalyl derivative Needles

C₂O₂(NH NH C₂H₄NO₂)₂. Formed from the hy drazide and oxalic ether Yellow needles, sol. hot nitrobenzene.

m-Nitro phenyl-hydrazine $C_8H_4(NO_2)NHNH_2$ [93°] Prepared in the same way as the o-compound (Bischler a Brodsky, B 22, 2809) Canary yellow needles Reacts with ketonic compounds, yielding their m nitro phenyl hydrazides, with the following melting points from aldehyde [98°], from acctone [112°], from benzoic aldehyde [118°], from acetophenone [160°], from benzil [158°]; and from aceto acetic ether [117°]

Salts -B'HCl -B'2H2SO, yellow crystalline groups, v sol hot water

Acetyl derivative [145°] Plates Di-acetyl derivative [150°] Tables (a)-Acetyl-(β) bensoyl derivative C₆H₄(NO₂)NBz NHAc [187°] Formed from the acetyl derivative and Bz₂O at 160° lowish aggregates of crystals

(a)-Bensoyl-(β)-acetyl derivative C.H.(NO2)NAc NHBz [147°] Formed from the benzoyl derivative, Ac.O, and NaOAc. Needles (by sublimation).

[151°] Needles Bensoyl derivative Di-bensoul dersyative. [1530]. Plates. Di-nitro di-phonyl-hydrazine

M. nitre di. phenyi-hydrasine

O.H., NH NH C.H.(NO.), [124] [120°] Formed

trom O.H.(Ol(NO.)), and phenyi hydrazine (Willgerodt, J. pr. [2] 87, 350, 40, 252, 42, 132)

Red plates Converted by shaking with HgO
into C.H., N., C.H.(NO.), [117°] On boiling with
alcohol it yields C.H., N., C.H.(NO), [178°], boil
ing HOAc forms C.H., N., C.H.(NO)(NO.) [175°]

Dim nitro s di phenyi hydrasine

(D.H.(NO.)), N.H. [220°] Formed from di-

[220°] $(C_6H_4(NO_2))_2N_2H_2$ Formed from dinitro azobenzene and cold alcoholic ammonium sulphide (Lermontoff, B 5, 236) Yellow needles

Tri nitro di phenyl-hydrazine C₆H₃NH NHC₆H₂(NO₂), [1 2 4 6] [185°] Formed from C₆H₂Cl(NO₂), and phenyl hydrazine hydrochloride (Willgerodt, *J pr* [2] 37, 346, 40, 264, Fischer, *A* 190, 132, 253, 1) Red crystals, melting at 175°-180° when slowly heated, but 183°-185° when quickly heated By boiling with MeOH it is converted into the compound C_cH_1 , N_1 , C_cH_2 (NO₂), [218°] On heating with HOAc it yields C_cH_1 , N_2 , C_cH_2 (NO₂), (NO) [248°] (Freund, B 22, 1663), which yields a mono sulphonic acid crystallising from water in yellow needles, not melted at 360°

o NITRO PHENYL - HYDRAZINE SUL-PHONIC ACID C_eH₂(NO₂)(SO₂H) NH NH Formed from o nitro diazobenzene sulphonic acid and a well cooled, strongly acid, solution of SnCl, (Nietzki a Lerch, B 21, 3220) —HA'HCl

m Nitro phenyl hydrazine sulphonic acid [3 6 1] C₆H₃(NO₂)(SO₃H) NH NH₂ Formed from nitro diazobenzene sulphonic acid and cold SnCl, (Limpricht, B 18, 2194) Yellow needles (con taining aq) -KA'1 aq -BaA', 1 aq -PbA', 4aq

NITRO PHENYL HYDROXYLAMINE v

HYDROXYLAMINE DERIVATIVES

DI NITRO DI PHENYL HYPOPHOSPHOR OUS ACID (C.H.NO2)2PO OH [268°] Formed from Ph.PO₂H, nitro acid, and H₂SO₄ (Dörken, B 21, 1513) Yellow pp, v sol water —NH₄A' [260°] —KA'2aq —BaA'₂6aq —PbA'₂—AgA'

NITRO PHENYL & INDAZINE CARBOXY-LIC ACID $C_{\bullet}H_{\bullet}(NO_{2}) < \stackrel{C(CO_{\bullet}H_{5})}{<} N$

Formed by the action of alcoholic potash on the red needles [183°] formed from di nitro-phenyl acetic ether and diazobenzene (V Meyer, B 22, 319, A 264, 149) Sulphur yellow needles, v sl sol alcohol Reduced by SnCl, to a dihydride [235°]

Methyl ether MeA' [192°] Converted by HNO, into C15H10N4O6 [281°], and by H₂SO₄ into a sulphonic acid (Strassmann, B 23, 714)

Ethylether EtA' [158°] Needles NITRO-NITRO-DI-PHENYL-KETONE BENZOPHENONE

DI-NITRO-PHENYL-MALONIC ETHER C_eH_s(NO₂)₂.CH(CO₂Et)₂. [51°] Formed from sodium malonic ether and C_eH₃Br(NO₂)₂ (Von Richter, B 21, 2472) Pale-yellow prisms.

m-NITROPHENYL MERCAPTAN C.H.(NO2) SH Formed by the action of alcoholic potash on the ether formed from potassium xanthate and m-diazobenzene (Leuckart, J pr. [2] 41, 197). Yellow liquid with nasty smell

p-Nitro-phenyl mercaptan C.H.(NO.)SH. Formed from O.H.Cl(NO.) and alcoholic KSH (Willgerodt, B. 18, 881). Crystals

Di nitro-phenyt mercaptan C.H.(NO)2SH

1810 | Formed from O.H.cl(NO.); and KHS (Willgerodt, J 1884, 974) | Needles Ethers (Willgerodt, B 18, 380) MeA'. [126°] — EtA' [118°] — PrA' [94°] — PrOH.A'. [72°] — O.H.CH.A'. [128°] — EZA' [118°]

Di-nitro-phenyl-mercaptan [195°] Formed by heating C₆H₂(NO₂)₂SCN with conc H₂SO₄ (Austen a Smith, Am 8, 90) Yellow powder_

Tri-nitro phenyl mercaptan C.H.(NO2)2SH [6 4 2 1] [114°] Formed from C.H.20(NO₂), and alcoholic KSH (W) Small yellowish needles Explodes at 115°—KA' brown needles

O-NITRO PHENYL-METHACRYLIC C_eH₄(NO₂) CH CMe CO₂H. [165°] Formed by hydrolysis of its ether, which is prepared from methyl phenyl methacrylate and HNO. Formed also from phenyl isobutyric acid and HNO, (Edeleanu, B 20, 621, C J 53, 559) Crystalline powder, yielding o nitro benzoic acid on oxidation

m Nitro phenyl-methacrylic acid Formed from m nitro benzoic aldehyde by heating with sodium propionate and propionic anhydride (Von Miller, B 23, 1900) White powder, v sol hot alcohol

p-Nitro phenyl methacrylic acid Formed in the same way as the o isomeride (E) Crystals —AgA' white needles Methyl ether MeA' [115°] Plates

m NITRO-PHENYL METHACRYLIC ALDE-HYDE C₆H₄(NO₂) CH CMe CHO [83°] Formed from m nitro-benzoic aldehyde, propionic alde hyde, and dilute (10 p c) aqueous NaOH (Miller a Kinkelin, B 19, 530) Thin prisms (from alcohol) Aniline yields oily C, H, (NO2) CH NPh and crystalline C.H. (NO.) CH(NHPh). [170°] Tin and HCl yield a base C. H.I.N [98°], whence Ac O forms C. H., Aco [146°], and benzoic alde hyde produces C. H., N(CHPh) [73°] Phenyl hydraside C. H., N.O. [135°]

NITRO DI PHENYL METHANE C, H, NO,

se C.H. CH. C.H.NO.

o compound Formed from o nitro benzyl chloride, benzene, and AlCl, (Geigy a Kenigs, B 18, 2402) Oil

m-compound [141°] Formed from m nitrobenzyl alcohol and conc H.SO. (Becker, B 15, 2091) Oil, sol alcohol

Formed by either of p- compound [31°] the above methods (Basler, B 16,2716, Manns, C C 1888, 1363) Prisms, v sol. alcohol

m-Nitro-tri-phenyl methane CHPh, 0.H,NO: [90°] Formed from m-nitro benzoic aldehyde, benzene, and H,SO. (Tscha cher, B 19, 2463, 21, 188) Crystals (from ligroïn

[93°] Formed p-Nitro-tri-phenyl-methane in like manner (Baeyer a Löhr, B 23, 1622)

C, H, (NO2), Di-nitro-di-phenyl-methane By nitrating diphenyl methans Doer $(B \ 5, 795)$ obtained two compounds of this formula, melting at 183° and 172°, while Staedel (A 194, 868) obtained the (a)- compound [183°] and a (s) isomeride [118°] By nitrating m-nitro diphenyl-methane Becker (B 15, 2092) obtained a fourth isomeride [94°], while Basler (B 16, 2719) got a fifth isomeride [175°] by the nitration of p-nitro-di-phenyl-methane

Tri-nitro-tri-phenyl-methane CH(C,H,.NO2), [207°] Formed by nitrating tri phenyl-methane

(E a O Fischer, A 194, 254, of Hemilian, B. 7, 1203) Scales (from benzene)

[1720] Tetra - nitro - dı - phenyl - methane Formed from CH_Ph₂ and fuming HNO₂ at 0° (Staedel, A 218, 339) Long pointed needles DI-NITRO-DI PHENYL-METHYL-AMINE

C.H.(NO.)NMe C.H., [167°] Formed from C.H.(Cl(NO.)), and C.H.,NMe, or C.H.,NHMe (Leymann, B 15, 1235) Reddish needles NITRO DI PHENYL METHYL CARBINOL

C_eH₄(NO₂) CPh(OH) CH₃ [107°] Formed from 24-d1 phenyl ethane and HNO₃ (Anschutz a Formed from White prisms, yielding an Romig, B 18, 664)

acetyl derivative [86°

O NITRO PHENYL TRIMETHYLENE GLY. COL C₆H₄(NO₂) CH(OH) CH₂ CH₂(OH) Formed from o nitro benzoic aldehyde, acetic aldehyde, and an alkalı (Baeyer a Drewson, B15, 2861) Colourless needles

NITRO PHENYL TRIMETHYLENYL KE TONE CARBOXYLIC ACID

C_eH_s(NO₂) CO C(CO₂H) < CH₂ [176°]

tained from its ether, which is produced by the action of ethylene bromide on sodium p nitro benzoyl acetic ether (Perkin a Bellinot, B 18. Colourless needles -AgA' amorphous

Ethyl ether EtA' [84°] Prisms NITRO-PHENYL-METHYL KETONE v NITRO-ACETOPHENONE

p-NITRO-PHENYL METHYL-OXAZOLE $\begin{array}{c}
\mathbf{CH} \mathbf{C}(\mathbf{C}_{6}\mathbf{H}_{4}\mathbf{NO}_{2}) \\
\mathbf{N} = -\mathbf{C}(\mathbf{CH}_{3}) - \mathbf{O}
\end{array}$ [157°] Formed by the action of conc HNO, on the base obtained from acetamide and bromo acetophenone (Lewy, B 21, 925) Yellow needles, v sol hot alcohol Yields an amido- derivative [115°]

p-NITRO PHENYL (β)-METHYL PIPERID $\mathbf{INE} \ \mathbf{C_sH_4(NO_2)} \ \mathbf{NC_5H_9Me} \quad [61^{\circ}]$ Formed by heating (3) methyl piperidine with C.H.Cl(NO₂) at 150° (Lellmann a Buttner, B 23, 1389) Golden plates (from alcohol) -B'HAuCl, 2aq

Di-nitro phenyl (3) methyl piperidine [67°] Formed in like manner, using the compound

C₆H₃Cl(NO₂)₂[1 2 4] Yellow needles

O-NITRO DI PHENYL-METHYL-PYRAZOLE $C_{10}H_{10}N_3O_2$ to $C_0H_4(NO_2)$ $C \gtrless_{CH}^{N} \stackrel{NPh}{CMe}$ [105°] (285° at 70 mm) Formed by heating its carboxylic acid [218°] (Knorr a Jödicke, B 18, 2261) Iridescent plates [95°], slender needles, or thick prisms [105°]—B'₂H₂PtCl₆ [198°] p Nitro di-phenyl-methyl-pyrazole

C₁₆H₁₈N₃O₂. Formed by heating its carboxylic acid [202°] Oil —B',H,PtCl₈ slender needles Tri-nitro di phenyl methyl pyrazole

 $C_6H_4(NO_2)$ $C < N N(C_6H_4NO_2) > [178°]$ Formed by nitrating di-phenyl methyl pyrazole (Knorr a Laubmann, B 22, 174) V sl sol alcohol

NITRO-DI-PHENYL-METHYL PYRAZOLE CARBOXYLIC ACID

 $C_0H_4(NO_2)$ $C < N N(C_0H_3) - CMe$. The ethers of the o- acid [218°] and of the p-acid [202°] are respectively formed by heating o- and p- nitrobenzoyl-acetoacetic ether with phenyl-hydrazine in HOAc (Knorr a Jodicke, B 18, 2257) The co-ether melts at 146° and the p-ether at 128° Both crystallise well

m-NITRO-PHENYL-DI-METHYL-PYRID INE DICARBOXYLIO ETHER $C_{10}H_{20}N_2O_4$ is $C_6H_4(NO_4)$ $C_5NMe_4(CO_4Et)$, [65°] Formed from its dihydride and fuming HNO₄ (Lepetit, G 17, Colourless crystals (from alcohol) -461) [202°] Orange years of Colourless needles Orange yellow needles -B'HNO, [130°]

NITRO PHENYL-DI METHYL PYRIDINE DIHYDRIDE DICARBOXYLIC ETHER

 $C_8H_4(NO_2)$ C_8NH Me $(CO_2Et)_2$ Formed from nitro benzoic aldehyde, acetoacetic ether, alco hol, and NH, (Lepetit, G 17, 460, B 20, 1341)

[120°] Yellow tables o isomeride

ĭ161°i Tables m- isomeride [118°-122°] p isomeride

m NITRO-PHENYL METHYL-QUINOLINE

C₆H₄ CH CMe N C C₆H₄NO₂ [145°] Formed by heat anilinewith m nitro a methyl cinnamic aldehyde and conc HClAq (Miller a Kinkelin, B 19, 531) Small plates, v sol hot alcohol -B'HCl -B'2H,PtCl, long needles

DI NITRO PHENYL (a) NAPHTHYLAMINE C_{1e}H₁₁N₃O₄ te [4 2 1]C₈H₁(NO) NHC₁₀H [190 5°] Formed from (a) naphthylamine and $[4\ 2\ 1]C_sH_{*}(\mathrm{NO}\,)\ \mathrm{NHC_{10}}H$ $C_0H_3Br(NO_2)_2$ [72°] (Heim, B 21, 2302) Orange red needles (from alcohol) Conc H.SO, forms

a dark blue solution

[770] Prepared by nitration of Isomeride phenyl (a) naphthylamine (Streiff, B 13, 1853)

Di nitro phenyl (β) naphthylamine (H), [179°] (E) Prepared by the action of C₆H₃Br(NO₂)₂ or C₆H₃Cl(NO₂), on (β) naphthyl amine (Heim, B 21, 589, Ernst, B 23, 3429) Prisms By nitration of phenyl (3) naphthyl amine Streiff obtained C₁₈H₁₂(NO₂)N [85°] and C₁₆H₁₁(NO₂)₂N [192°-195°], both crystalline

Tetra nitro phenyl naphthylamine C₁₀H₃(NO₂),NHC₆H₃. The (a) compound [162 5° and the (b) isomeride [253°] are formed from aniline and the corresponding bromo tetra nitro naphthalenes (Merz a Weith, B 15, 2712) Both crystallise from benzene in orange needle: (containing benzene)

DI-NITRO-PHENYL-(a) NAPHTHYL HY DRAZINE C16H12N4O4 [181°] Formed from (a) chloro di nitro benzene and (a) naphthyl hy drazine (Willgerodt, J pr [2] 43, 181) Rec (B)-Naphthylamine yields an isomeride prisms

Tri - nitro - phenyl - (a) naphthyl hydrazine C18H11N5O6 [176c] Got from an alcoholic so lution of picryl chloride and (a) naphthyl hy drazine (W) Occurs in a red stable modification and an unstable yellow one (8)-Naphthylamin forms an isomeride [175°] also occurring in two

DI - NITRO - PHENYL - (β) - NAPHTHY **OXIDE** C₁₀H₇ O C₆H₈(NO₂)₂[1 2 4 [95°] Former from C₆H₂Cl(NO₂)₂ and (\$\beta\$) naphthol (Ernst, \$B\$ 23, 8430) Yellow needles (from alcohol)

NITRO-PHENYL NITRO-BENZYL OXIDI C_eH₄(NO₂) O CH₂·C_eH₄(NO₂) The compound formed from p nitro benzyl chloride, o nitro phenol, and alcoholic potash melts at 129° , th pp isomeride at 183° (Kumpf, B 17, 1077, App 180m 224, 107

Di-nitro-phenyl nitro benzyl oxide. [4 2 1]C,H,(NO₂),O CH,O,H,NO₂[1 4] [201°] an 6 2 1]C,H,(NO,),O CH, O,H,NO,[1 4] [1879 have been prepared (Staedel, B. 14, 899, Kumpf) They yield di nitro aniline and p nitro benzyl | alcohol [91°] on heating with alcoholic am

Tri nitro phenyl nitro benzyl oxide $[6 \stackrel{4}{2} 1]$ C₆H₂(NO₂), O CH₂ C₆H₄NO₂[1 4] [108°]. Long thin needles (K)

DI NITRO-DI-PHÉNYL OXIDE

[135°] Formed by nitrating di-C_{1,}H₈(NO₂)₂. [135°] Formed by nitrating diphenyloxide (Hoffmeister, A 159, 191) Needles

Di nitro di phenyl oxide C_eH₂(NO₂)₂ OC_eH [71°] Formed from C₆H₃Cl(NO₂), and PhOK (Willgerodt) Needles

Tri nitro-di phenyl oxide [4 2 1] C₆H₄(N O_2)₂ O C₆H₄(N O_2) Formed from C₆H₂Cl(NO₂)₂ and C₆H₄(NO₂)(OK) The o com pound (x=2) melts at 119°, the p isomeride (x=4) at 114° (Willgerodt a Hüetlin, B 17, Both are v sol benzene

Tetra nitro di-phenyl oxide

[6 4 2 1] $C_sH_s(NO_g)_s$ O $C_sH_s(NO_g)[1\ x]$ Formed from $C_sH_s(2)(NO_g)_s$ and $C_sH_s(NO_g)(0K)$ The o compound (x=2) melts at 173° and the p-150 meride at 153° (W a H) Both are crystalline Formed

Tetra nitro di-phenyl oxide {C₆H₃(NO₂)₂}₂O [195°] Formed by the action of C.H.Cl(NO2), on C₆H₄(OK)(NO₂)₂ (Willgerodt, B 13, 887) Thick crystals, almost insol alcohol

NITRO PHENYL-OXY-ACETIC ACID v NI

TRO MANDELIC ACID

p NITRO-PHENYL OXY BUTYL KETONE ANHYDRIDE CARBOXYLIC ACIDC, H,1(NO2)O. o<CH, CH, CH, CH, SCO,H Formed from trimethylene biomide and sodium p nitro benz oyl acetic ether (Peikin, jun, B 18, 954, C J 51, 735) Melts at 172° when crystallised from benzene, 183° when crystallised from water—

AgA' light yellow needles Ethyl ether EtA' [63°] Lustrous yellow monoclinic crystals, abc = 235311853,

 $\beta = 80^{\circ} 42^{\circ}$

m-NITRO PHENYL PARACONIC $C_{11}H_9NO_{\bullet}$ s.s $C_6H_4(NO_2)$ $CH < C_{OCO}^{CH(CO_2H)} > CH$.

[171°] Formed by heating m nitro benzoic al dehyde with Ac,O and NiOAc at 125' (Salo monson, B 18, 2154, R T C 6, 1) Crystals Yields with baryta the salt $C_{11}H_{\theta}NO_{\tau}Ba$ The cor responding p- isomeride melts at 163° (S , cf Erdmann, B 18, 2742)

p NITRO-PHENYL PENTINOIC ACID C.H.(NO.) CH CH CH CH CO H [271°] Formed from p nitro cinnamic aldehyde, Ac₂O, and NaOAc (Einhorn a Gehrenbeck, B 22, 45, A 253, 357) Formed also by oxidising the ketone OgH4(NO2) CH CH CH CH COMe with NaOCl Yellowish needles (from alcohol) For tetrabromide [254°] —AgA' flocoulent pp Forms a

[118°] Plates Ethyl ether EtA' o Nitro-di-phenyl pentinoic acid Natrale C₆H₃ CH CH CH C(C₆H₄NO₂) CN [206°] Formed from p nitro benzyl cyanide, cinnamic aldehyde, and NaOEt (Remse, B 23, 3135) Needles

p NITRO-PHENYL PHENYL-(β)-AMIDO-PRÔPIONIC ACID

C.H.(NO.) CH(NHPh) CH. CO.H [122°] Formed from aniline and C.H.(NO.) CHBr CH., CO.H (Basler, B. 17, 1500) Yellow crystals

Ethyl ether EtA' [78°] Crystals
DI - NITRO - PHENYL - PHENYLENE - DI -

AMINE C.H. (NO.). NH C.H. NH. [172°]. Vor. III

Formed from C_eH₂Cl(NO₂)₂[1 2 4] and phenylene-m-diamine (Leymann, B 15, 1237)

The fol-

lowing compounds have been prepared by Rapp (A 224, 158), the NO₂ being in the p-position:

C.H.(NO.)O PO(OH), [1129], (C.H.(NO.)O PO(OH), [1129], (C.H.(NO.)O).PO OH[133°], (C.H.(NO.)O).PO OEt [135°], and (C.H.(NO.)O).PO [155°] Tri o int

Tri o mitro tri phenyl phosphate melts at 126° (Engelhardt a Lat

schinoff, Z 1870, 230)
TRI NITRO TRI-PHENYL PHOSPHINE OXIDE OP(C₆H₄NO₂)₃ [243°] Got by nitrating tri phenyl phosphine hydrate (Michaelis a Got by nitra-Soden, B 17, 921, A 229, 324) It is accompanied by an isomeride [68°

m NITRO PHENYL PHTHALIMIDE

 $C_{\bullet}H_{\bullet} < CO \longrightarrow C$ [243°] Prepared by heating phthalic anhydride with m nitro aniline (Gabriel, B 11, 2261) Needles, v sl sol EtOH

NITRO PHENYL PIPERIDINE lowing compounds are formed by the action of piperidine upon the corresponding halogen de matives of nitro- and di nitro benzene respec tively (Lellmann, B 20 680, 21, 2281) [1 4] C₆H₄(NO₂) NC₂H₁₀ [81°] red prisms, yielding the salts B'HCl and B'₂H₂PtCl₆ [1 2 C₅H₄(NO₂) NO₅H₁₀ [105 5°] yellow plates, yielding the salts B'HCl and B'₅H₂PtCl₅ [4 2 1] C₅H₃(NO₂)₂ NC₅H₁₀ [92°] orange needles o NITRO PHENYL-PROPIOLIC ACID

 $C_9H_3NO_4$ 16 $C_6H_4(NO_2)$ C C CO_2H Formed from $C_6H_4(NO_2)$ CHBr CHBr CO H (or 1ts ether) and aqueous NaOH (Baeyer, B 13, 2258, Muller, A 212, 127) Needles (from hot water), decomposing at 156° On boiling with water it gives o mitro phenyl acetylene Boiling alkalis yield 15 tin Reduction with glucose and alkalis produces indigo FeSO₄ also reduces it, in alkaline solution, to indigo white Its Na salt boiled with aqueous KCN and glucose yields indigo, even in presence of much HCN (Michael, J pr [27 35, 254)

[61°] Ethyl ether EtA' Tables verted by conc H SO, into isatogenic ether (q v)

p-Nitro-phenyl propiolic acid [181°] (M), [198°] (D) From C.H. (NO.) CHBr CHBr CO_Et and alcoholic potash (C Muller, A 212, 127, Drewson, A 212, 154, Perkin, C J 49, 442). Yields p nitro phenyl acetylene and CO2 on distilling with steam —AgA' amorphous powder

Ethyl ether EtA' [126°] Needles

O NITRO & PHENYL PROPIONIC ACID $[112^{\circ}]$ C_bH₄(NO₂) CH CH CO₂H Formed from (2, 4, 1) nitro amido phenyl propionic acid by elimination of NH₂ (Gabriel a Zimmermann, B 12, 600, 13, 1680) Yellow crystals —AgA'

[118°] m-Nitro-phenyl propionic acid Formed in like manner from the (3, 4, 1)-nitroamido-phenyl propiomo acid (Gabriel, B 15, 845) Yellow needles, sl sol water

p Nitro-β-phenyl-propionic acid [164°] Formed, together with the o acid, by nitration of (8) phenyl propionic acid (Glaser a. Buchanan, 1869, 193, Beilstein a Kuhlberg, A 163, 132) — CaA', 2aq — BaA', 2aq small needles. Ethylether EtA'

o-Nitro a phenyl-propionic acid C.H.(NO.) CHMe CO.H [110°]. Formed, together with the p- isomeride [88°], by nitration of a-phenyl propionic soid (Trinius, A 227, 262) The o acid forms the salt CaA', 2aq, the p-acid gives CaA', 2aq and BaA', 2aq

Di-nitro-phenyl propionic acid C_cH_s(NO₂)₂ CH₂ CH₂ CO₂H [127°] Formed by nitration of β phenyl-propionic acid (G a Z)

Ethylether EtA' [32°] Needles a-NITRO PHENYL PROPYLENE

C.H. CH C(NO2) CH. Formed from $[64^{\circ}]$ benzoic aldehyde, nitro ethane, and ZnCl2 at 140° (Priebs, \mathring{A} 225, 354), yellow needles

Di nitro phenyl propylene C_oH₄(NO₂) CH C(NO₂) CH, The o compound [77°] is formed, together with the p isomeride [115°], by nitrating a nitro phenyl propylene (T)

Di-nitro phenyl-propylene C₆H₃(NO₂)₂CH CHMe [118°] Formed from C_sH, CH CMe CO₂H and HNO₃ (Edeleanu, B 20, 622) Yellowish needles

m-MITRO-PHENYL PYRIDYL-ETHYLENE C₆H₄(NO₂) CH CH C₅H₄N [120°] Formed from m nitro benzoic aldehyde and methyl pyridine (Schuftan, B 23, 2716) Plates — B'2H,PtCl, [240°] -Mercury double salt B'HClHgCl, [211°] -Picrate yellow plates

TETRA-NITRO TETRA-PHENYL PYRROLE NH(C C₆H₄NO₂)₄ Formed from tetra pyrrole and HNO₂ (Fehrlin, B 22, 554) Formed from tetra phenyl Yellow needles (from HOAc), decomposing at 123°

(a) NITRO (Py 1) PHENYL QUINOLINE H₁₀N₂O₂ [187°] Formed together with a C₁₅H₁₀N₂O₂ smaller quantity of a (B) isomeride [118°] and a little of a (γ) isomeride [135°] by nitration of (Py 1)-phenyl-quinoline $C_{\bullet}H_{\bullet} < {\rm CPh} \ {\rm CH} \ ({\rm K\"{o}nigs}$

a. Nef, B 20, 624) They are all crystalline m-Nitro-(Py 8)-phenyl-quinoline

CH' CH'CH' NO' [124°] Obtained by heating m nitro-cinnamic aldehyde with aniline and HClAq at 140° (Miller a Kinkelin, B 18, White needles -B'HCl -B'2H2PtCl

Tetrahydride O.H. CH. CH. NH CH C.H.NO. [101°] Tables Yields a nitrosamine [71°] -

B'HCl silky needles

Nitro (B 2) phenyl-quinoline C1.H10N2O2 [173°] Formed, as well as a di nitro derivative [208°], by the nitration of (B 2) phenyl-quinoline CPh CH CH C, H, N (La Coste a Sorger, A 260, 28)

-B',H.PtCl, yellow needles
DI-NITEO-DI-PHENYL-SUCCINIC ACID $C_{16}H_{14}O_4(NO_2)_2$. The (a)- compound [226°] and its (β)- isomeride are formed by nitrating (a)- and (β)-di-phenyl succinic acid respectively (Reimer, B 14, 1804) Both give p-nitro benzoic acid on oxidation

DI-NITRO-DI-PHENYL-SULPHAZIDES

O,2H,(NO,)NH NH SO,O,H,NO,? Compounds formed by the action of SO2, nitrous acid, and alcohol on the nitro-anilines (Limpricht, B 20. 1241). The o, m-, and p- compounds melt at 150°, 162°, and 160° respectively. They yield They yield nitrogen, nitro benzene, and nitro benzene sulphinic seid on boiling with baryta
DI-p-NITRO DI-PHENYL DISULPHIDE

(C.H., NO.),8, [181°] (W), [170°] (L) Formed by oxidation of p nitro phenyl mercaptan (Will-gerodt, B. 18, 888), or by boiling with alcoholic

potash the product of the combination of potassium xanthate with p nitro diazobenzene (Leuck art, J pr [2] 41, 199) Prisms (from HOAc)

Tetra nitro-di-phenyl-sulphide $S(C_4H_4(NO_2)_2)_2$ [193°] Obtained from [1 ° 4] $C_8H_4(I(NO_2)_2)_2$ and alcoholic KSH (Beilstein a Kurbatoff, B 11, 2056, Willgerodt, B 12, 768) Yellow needles An isomeric body [245°] is formed by the action of H2SO, and fuming HNO, on C₆H₅(NO₄) SCN (Austen a Smith, Am 8,91)

Tetra nitro-di phenyl disulphide S₂(C₈H₃(NO₂)₂)₂. Obtained by oxidising [4 2 1] C₈H₃(NO₂)₂SH (Willgerodt Bn 2 527) Yellow

needles, exploding at about 280°

dles, exploding as applications of the phone $C_6H_3(NO_2)_2$ S $C_6H_2(NO_2)_3$ [217°] Formed from $C_6H_3Cl(NO_2)_2$, K.S., and $C_6H_2Cl(NO_2)_4$ (W) Thick crystals (from HOAc)

Hexa nitro-di-phenyl sulphide

 $S(C_oH_2(NO_2)_3)_2$ [226°] Formed from picryl chlorate and K_2S (W) Golden plates (from HOAc) DI NITRÒ-PHENYL SULPHOCYANIDE

[139°] C₆H₃(NO₂)₂SCN Formed by heating [124]C₆H₂Br(NO₂)₂ with potassium sulphocyanide in MeOH (Austen a Smith, Am 8, 89) Buff yellow crystals (from chloroform)

NITRO DI PHENYL SULPHONE C₆H₆ SO₂ C₆H₆NO [92°] Formed by heating di phenyl sulphone with fuming HNO, (Gericke, A 100, 208) Minute crystals

Di nitro di phenyl sulphone

 $(C_6H_4(NO_2))_2SO$ [164°] (G), [197°] (S a. N) Formed by nitrating di phenyl sulphone (G) and by the action of SO, on nitro benzene (Schmid a Nölting, B 9, 79) Small tables

Tetra nitro di phenyl sulphone (C₆H₃(NO₂)₂) SO [241°] Prepared by oxidising the corresponding sulphide [193°] (Beilstein a. Kurbatoff, A 197, 78) Yellowish prisms

p NITRO DIPHENYL p SULPHONIC ACID C,H,(NO2) C,H,SO,H Prepared by sulphona tion of p-nitro diphenyl or by nitration of diphenyl p sulphonic chloride (Gabriel a Damberger, B 13, 1408) — NaA' — CuA', 4sq — BaA'24aq small needles

Chloride C, H, (NO2) SO Cl [1789]. Amide C₁₂H₈(NO₂) SO₂NH₂ Ethyl ether EtA' [169° [228°]. [1690]

Nitro diphenyl disulphonic acid chloride $C_{12}H_{\gamma}(NO_2)(SO_2Cl)$, [130°] is formed, together with $C_{12}H_{\sigma}(NO_2)_2(SO_2Cl)_2$ [166°], by nitration of diphenyl disulphonic chloride (G a D).

DI NITRO DI-PHENYL SULPHOXIDE [116°] (C₆H₄(NO₂)),80 Formed from di phenyl sulphoxide, NaNO, and H.SO. (Colby a McLoughlin, Am 9, 70, B 20, 198) yellow crystals, v sol alcohol

NITRO PHENYL THIO CARBAMIC ACID

C.H.(NO2) CS OH The m compound Methyl ether MeA' [120°] is formed by boiling m nitro phenyl thio carbimide with MeOH (Steudemann, B. 16,

551) Colourless needles

Ethylether EtA' Them compound [115] and its p- isomeride [176°] are formed by boiling the corresponding nitro anilines with CS, alcohol, and potash (Losanitsch, B 15, 470, 16, Both are crystalline

m NITRO DI-PHENYL THIO-SEMICARBAZ. CeH4(NO2) NH NH CS NHPh [147°] Formed from phenyl thio carbimide and m.

nitro-phenyl hydrazine (Bischler a Brodsky, B

22, 2815) Dark yellow globular aggregates
m - NITRO - PHENYL THIO CARBIMIDE C_eH₄(NO₂) N CS [61°] (c 277°) Formed by he_ting m nitro phenyl thio ures with Ac₂O White needles (Steudemann, B 16, 549, 2331) DI NITRO PHENYL THIOPHENE

C₈H₁(NO₂) C₄SH₂(NO₂) [178°] Formed from phenyl thiophene and fuming HNO₂ (Renard, C R 109, 699)

R 109, 699) Amorphous yellow powder m NITRO PHENYL THIO UREA C,H,N,SO. ve C₆H₄(NO₂) NH CS NH₂ [158°] Formed from m nitro phenyl thiocarbimide (Steudemann, B 16, 550) Lemon yellow crystals

m Nitro di phenyl thio urea

C₆H₄(NO₂) NH CS NHPh [155°] Formed from m nitro aniline and phenyl thiocarbimide (Bruck ner, B 7, 1235, Losanitsch, B 14, 2365, Geb hardt, B 17, 3045) Small needles, sl sol cold alcohol

Di m nitro phenyl thio urea

CS(NH C₆H₄NO₂)₂ [160°] Formed from m-nitro aniline and m nitro phenyl thiocarbimide Yellow crystals (Bruckner, B 6, 1103, S)

o NITRO PHENYL P TOLUIDINE C₆H₄(NO₂) NH C₇H, [68°] Formed from ptoluidine and o bromo nitro benzene (Schöpff, B 23, 1842) Orange plates

Di nitro phenyl toluidine

[4 2 1] C₀H₁(NO₂), NHC₀H₁Me [1 x] Formed from toludine and C₀H₁Cl(NO₂), (Willgerodt, B 9, 980, Leymann, B 15, 1236) The o compound (x=2) melts at 102° , the p compound (x=4) at 137° The isomeric PhNH $C_{\bullet}H_{I}(NO_{2})_{2}Me$ formed from tri nitro toluene and aniline, melts at 142° (Hepp, A 215, 369) DI NITRO PHENYL TOLYLENE DIAMINE

C₆H₃(NO₂)₂NH C₆H₃Me NH₂ [184°] Formed from tolylene m diamine and [1 2 4] C.H.Cl(NO2)2

(Leymann, B 15, 1237) Red tables Formyl derivative [157°]

Acetyl derivative [164°]
NITRO PHENYL TOLYL KETONE

C,H, (NO)O [127°] Formed by the action of HNO, on phenyl tolyl ketone and on phenyl p tolyl methane (Plascuda a Zincke, B 7, 983, Milne, B 5, 685) Flat plates (from alcohol)

Di nitro phenyl m tolyl ketone C₁₄H₁₀(NO₂)₂O [145°] Formed from di nitro phenyl m tolyl methane [141°], HOAc, and CrO, (Senff, A 220, 236) Pointed needles (from al cohol) or short prisms (from HOAc)

Di nitro phenyl p tolyl ketone

 $C_6H_4(NO_2)$ CO $C_7H_6(NO_2)$ [127°] Formed, as well as the tri intro derivative [165°], by intra tion of phenyl p-tolyl ketone (Z a P) Needles m NITRO-PHENYL DI TOLYL METHANE

(O,H,),CH C,H,NO, [85°] Formed from m nitro benzoic aldehyde, toluene, and H.SO. (Tschacher, B 19, 2464, 21, 188) Crystals

Di nitro phenyl-tolyl methane C,4H,2(NO2)2. The three compounds of this composition got by nitrating phenyl o, m, and p-tolyl methane melt at 100°, 141°, and 137° respectively (Zincke, B 7, 986, Senff, A 220, 235) Tetra nitrophenyl p tolyl methane melts at 161°

NITRO - PHENYL - p - TOLYL - THIO - UREA CH, NH CS NH.C, H, NO H,,N,SO, 1.6 [148°] Formed from (2,4,1) nitro toluidine and phenyl thiocarbimide (Steudemann, B 16, 2836) Crystals Melts, after one fusion, at 167

m-Nitro phenyl-p tolyl thio-urea C.H.(NO) NH CS NH C,H, [173°] Formed from m nitro phenyl thiocarbimide and p toluidine (S) Needles, sl sol ether

Di nitro phenyl p tolyl thio urea $C_dH_4(NO_2)$ NH CS NH $C_rH_4NO_2$ [188°] Formed from m nitro phenyl thiocarbimide and (2,4,1)-

nitro toluidine (S) Crystals, sl sol alcohol

m NITRO PHENYL UREA C₂H₇N₃O₃ $C_0H_1(NO_2)$ NH CO NH₂ Formed from m nitro aniline and cyanogen chloride (Hofmann, A 67, 156, 70, 137) Yellow nee m Nitro di phenyl urea Yellow needles (from water)

 C_8H_5NH CO $NHC_8H_4NO_2$. [197°] (G), [187°] (B) Formed from m nitro di phenyl thio-urea and PbO (Bruckner, B 7, 1236) Formed also by boiling with benzene the compound PhNH CO N(C₀H₄ NO₂) N NPh [104°] obtained by the action of phenyl cyanate on phenyl cyanate (C, H, NO2) NH N NPh (Goldschmidt, B 21, 2578) Yellow needles

p Nitro di phenyl urea $[202^{\circ}]$ Formed by the action of phenyl cyanate on a solution of pnitro diazoamidobenzene in benzene (G) Yellow crystals (from alcohol)

m Nitro tri phenyl-urea

NPh, CO NHC, H,NO, [155°] Formed from
m nitro annine and NPh, COCI (Leilmann a Formed from Bonhöffer, B 20, 2121) Yellow needles isomeride prepared from p nitro aniline melts at 176°, and crystallises in bluish green tables

Di m nitro di phenyl urea CO(NH CeH, NO.), [233°] Formed from the thio urea and PbO (B)

Yellow needles (Losanitsch, B 16, 50)

Tetra nitro di phenyl urea CO(NH C₂H₄(NO₂)) Formed by nitration of di phenyl urea (Losanitsch, B 10, 690, 11, 1539) Yellow needles, melting above 200° (L) or at 189° (Hentschel, J pr [2] 34, 426) The green K salt C, H, K, N, O, explodes on heating p NITRO PHENYL VALERIC ACID

C.H. (NO.) CH. CHLt CO. Formed by heating p nitro benzyl ethyl malonic ether with aqueous KOH (Lellmann a Schleich, B 20, 438) Sparingly soluble powder, carbonising above 300°

p NITRO PHENYL VINYL MALONIC ACID C_sH₄(NO₂) CH CH CH(CO₂H)₂ [208°] Formed trom p nitro cinnamic aldehyde, malonic acid, and HOAc (Einhorn a Gehrenbeck, B 22, 45)

NITRO PHLOROGLUCIN C.H.(NO.)(OH).

Formed from phloroglucin and dilute HNO. (Hlasiwetz a Pfaundler, A 119,199) Reddish yellow scales, sl sol water

Tri nitro phloroglucin Cs(NO2)s(OH), Formed from tri nitroso phloroglucin, HNO, and H.SO. (Benedikt, B 11, 1376) Hexagonal crystals (containing aq) Its salts are explosive and Its salts are explosive and dye yellow With KCy it gives the isopurpurio acid reaction —KH_A'" aq —K_HA'" —K_A'"

NITRO PHTHALIC ACID CH_1(NO.)(CO.H)

Mol w 211 [220°] S (HOAo) 7 5 at 26° (Aguar, B 5, 899)

HNO, (Marignac, A 38, 7, Laurent, A 41, 110) -2 By nitration of phthalic acid (Hugo Muller, Z 1868, 257, Faust, A 100, 57, Mil er, A 208, 224) —3 By oxidation of nitro-naphthalene or of (a) di nutro naphthalene (Beilstein a Kurbatoff, B 12, 688, C C 1881, 859, A 202, 217, Guareschi, B 10, 294)

Properties. - Yellow orystals, v sol hot B B 2

water. Splits up below its melting point into water and anhydride when slowly heated

Salts — K₂A' aq — KHA'' aq — (NH₁)₂A'' - (NH₁)HA' 2aq — BaA'' xaq — ZnA'' 1½aq — PbA'' 1½aq — Ag₂A'' white powder

Mono ethyl ether EtHA" [111°]

Dr-ethyl ether Et₂A" [45°] Anhydride C₈H₃NO₈ [164°] (Graeff, B 15, 1127)

Nitro-phthalic acid C₈H₃(NO₂)(CO₂H), [4 2 1]

[161°]

Formation -1 Together with the preceding isomeride, by nitration of phthalic acid (O Miller, A 208, 224) —2 By the oxidation of di nitro-(β)-naphthol (Graebe a Drews, B 17, 1171)

Properties —Small pale yellow needles (con taining aq) Resolved at 165° into water and

its anhydride

 $-K_2A''$ —BaA'' 2aq —Ba₁₂ H_2A'' Salts Zn₁₂H₁A"₁₃2aq —Ag₂A' long colourless needles Mono ethyl ether EtHA"

Drethyl ether Et,A" [33°]

Anhydride C₈H₈NO₂ [114°] Di nitro phthalic acid C₆H₂(NO₂)₂(CO₂H)₂ [5 3 2 1] [226°] Formed by the oxidation of 'β'-di-nitro naphthalene or tetra nitro (α)naphthol with dilute HNO, (Beilstein a Kurbatoff, B 13, 354, A 202, 225, Merz a. Weith, B 15, 2728) Prisms—CaA"—BaA"

Mono-ethyl ether EtHA" [187° Di-nitro phthalic acid C_oH_o(NO₂)₂(CO₂H)₂ [6 3 2 1] [200°] Formed by heating 'β' bromo tetra nitro naphthalene with dilute HNO, (Meiz a Weith, B 15, 2728) Needles -BaA

Di nitro phthalic acid C₆H₂(NO₂)₂(CO₂H) Formed from nitro anisic acid, HNO, and H2SO, (Engelhardt a Latschinoff, Z [2] 7, 262) Tables

811 at 99° Prepared, together with an isomeride [260°] by heating isophthalic acid (100 g) with fuming HNO, (1 kilo) for 24 hours (Beyer, J pr [2] 22, 35, 25, 473, cf Storrs a Fittig, A 153, 285) Plates (containing 1½ aq)

Salts — K₂A''1\(\frac{1}{2}\)aq S (80 pc alcohol)

744 at 15° — Na₂A''aq S (80 pc alcohol)
 d2 at 15°
 Explodes above 160°
 — (NH₄)HA"

 MgA"5aq
 S 2 15 at 15°
 — CaA"3½aq
 S 72 at 15°

 Turned violet
 by light
 — SrA"4½aq

 S 47 at 15°
 — BaA"2½aq
 S 75 at 15°

 EnA"aq
 S 55
 — CdA"2aq
 S 75 at 15°

 D A"
 S 75
 — SrA"4½aq
 Pb₀OA"₄ — Cu₁OA"₂ — MnA" 5aq S 244 at 15° — Fe₁₄O₅A"₁₉ — CoA" 4½aq S 2 16 at 15° — N1A" 4½aq S 2 74 at 15° — Ag₂A" Explodes N1A" 4 1 aq above 100°

Methyl ether Me.A"
Ethyl ether Et.A" [122°].

Ethyl ether Et.A" [84°]

Nitro-isophthalic acid C.H. (NO.) (OO.H).

[481] [246°] (C), [259°]. Formed by oxidation of nitro-xylene (Claus, J. pr. [2] 38, 318, cf.

Wroblewsky, Bl [2] 34, 332, Noyes, Am. 10, 472) C,H,(NO2)(OO2H), 472) White needles (containing Saq), m sol cold water—BaA" 4aq (0).—BaA" 1½aq (N)—CaA" ½aq — MgA"6aq — PbA" 8aq (W)—Ag₂A" 7½aq pearly plates

Di-nitro-isophthalic acid C.H. (NO2)2(CO2H) [215°] Formed from isophthalic acid and fuming HNO at 180° (Claus) Needles (containing 5aq) — Na A" 2aq — K A" 2aq — Ba A" 7aq — CaA" 4aq. - MgA" 4aq: needles, v sol water.

NITRO-PHTHALIDE

 $\begin{bmatrix} 4 & 1 \\ 2 \end{bmatrix} C_6 H_3 (NO_2) < \begin{matrix} CO \\ CH_2 \end{matrix} > 0$ [141°] Formed by nitration of phthalide (Hoenig, B 18, 3447) Long needles Aqueous KOH yields C,H3(NO)(CH,OH)(CO,K) CrO, in HOAc oxi dises it to nitrophthalic acid [161°] The acid of which it is the anhydride melts at 129° isomeric nitro-phthalide [136°] is formed by oxidising (a) nitro naphthalene

NITRO-DIPHTHALYL C16H,NO. 1 e C.H. C.O. C.H.NO. [270°] Formed by heat ing nitro phthalide with phthalic unhydride and NaOAc (Graebe a Guye, A 233, 244)

needles (from HOAc)

NITRO-PIPERIDINE C.H. (NO2) Formed by treating piperyl urea with HNO. (S G 1 5) at -10°, pouring upon sodium carbonate and extracting with ether (Franchimont a Klobbie, R T C 8, 302) Colourless liquid, solidifying below -10° Volatile with steam

NITROPODOCARPIC ACID v PODOCARPIC

NITRO - PROPANE C.H., NO. te PrNO. (127°) (M a R), (131°) (P) SG 15 10108, 23 10023 MM 3819 (Perkin, C J 55, 689) Formed, together with propyl nitrite, by the action of silver nitrite on propyl iodide (V Meyer a Rilliet, B 5, 1029, A 171, 36, Pribram a. Handl, M 2,653, Cahours, C R 77,749) Oil — NaC3H6NO2 white powder

Iso nitro propane PrNO₂. (c 117°) Formed, together with an isomeride (44°), by the action of silver nitrite on isopropyl iodide (V Meyer a. Locher, B 7, 670, A 171, 39, Kiesel, J R 16, 135, Bl [2] 40, 72, Bn 1, 225) Oil, decom-

posed by HClAq at 100°

Di nitro propane CH, CH, CH(NO₂)₂ (189° cor) SG ²²² 1 258 Formed from bromonitro propane and KNO₂ (Ter Meer, A 181, 19), and by the oxidation of di propyl ketone (Chan cel, C R 96, 1466, Kurtz, A 161, 208) KA' -AgA' explosive lamine

Iso-di nitro propane (CH.) $C(NO_2)_2$ [58°] (187° uncor) Formed by oxidation of propylpseudonitrole $(CH_1)_2C(NO)(NO_2)$ (Meyer a. Locher, B 7, 1613) Formed also by the action of nitric acid on isobutyric and isovaleric acids (Bredt, B 15, 2822) White crystals, volatile with steam

NITRO PROPENYL BENZOIC ACID $C_6H_3(NO_2)(C_3H_5)CO_2H[3 4 1]$ [155°] Formed by boiling nitro oxypropyl benzoic acid with aqueous HCl (S G 1 10) for a long time (Widman, B 15, 2551, 16, 2569) Short needles— NH,A'—CaA', 2aq S 555 at 16°—BaA', 8 daq S 425 at 18°—CuA', aq —AgA' slender needles S NITEO-PROPIONIC ACID C,H,NO, 16

CH₂(NO₂) CH₂ CO₂H [67°] Formed from 8 10d0 propionic acid and AgNO₂ (Lewkovitch, J pr [2] 20, 165) Scales (from chloroform)

Ethyl ether EtA' (c 168°) V.D 485 (calc 5 09)

DI-NITRO-PROPYL-ANILINE C,H,,N,O, t e C₆H₅(NO₂)₂NHC₅H₇[4 2 1] [95°] Formed from propylamine and C₆H₅Br(NO₂)₂, or by oxidising the following body (Van Romburgh, R T C. 4, 191, 8, 252) Yellow needles

Di nitro di propyi aniline C₄H₄(NO₂),N(C₄H₂), [4 2.1], [40°] (Rounburgh, R. T. G. 8, 252).

Tri-nitro-propyl-aniline C,H,(NO,),NH C,H, [59°] Formed from NH₂C₃H, and C₄H₂Cl(NO₂), Yields with HNO, the nitramine C.H.(NO.),N(NO.)C.H. [97°] NITRO-ISOPROPYL BENZENE v NITRO-

Di nitro p di propyl-benzene C.H.Pr. (NO.). Formed from di propyl benzene and fuming HNO, (Korner, B 11, 1865, A 216, 226) Plates, volatile with steam

Tri nitro m di-isopropyl benzene

C₈HPr (NO₂), [111°] Yellow needles (Uhlhorn, B 23, 31427

NITRO-PROPYL-BENZOIC ACID v NITRO-

n CUMINIC ACID

NITRO ISOPROPYL CINNAMIC ACID

[4 2 1] C₆H₃Pr(NO₂) CH CH CO H Nıtro cumenyl acrylic' acid [157°] Formed by nitration of propyl cinnamic acid (Einhorn a Hess, B 17, 2016, Widman, B 19, 258) Needles, v sol alcohol Yields o nitro cuminic aldehyde on oxidition by KMnO

Nitro isopropyl cinnamic acid

[4 3 1] C_bH₃Pr(NO_b)C₂H₂CO₂H [141°] Formed by heating m nitro cuminic aldehyde (4 pts) with Ac,O (5 pts) and NaOAc (3 pts) at 175° for 4 hours (Widman, B 19, 413) Tables
Forms a dibromide [184°] — KA' (dried at 100°)
— NaA' 3aq — BaA' 5\aq — CaA', 3aq
Ethyl ether EtA' [59°] Tables.

Nitro-n propyl-cinnamic acid

[4 2 1] C₆H₃Pr(NO)C₂H₂CO₂H [123°] Formed, in small quantity, in the nitration of isopropyl cinnamic acid (Widman, B 19, 273) tion by alkaline kMnO, it yields nitro n cuminic acid and nitro cuminic acid Bromine forms a di bromide [171°]

DI NITRO PROPYL-THIOPHENE C,HPr(NO) S Formed by nitration (Rufli, B

20, 1712) Oil

NITRO PROTOCATECHUIC ACID C.H.NO.

Methyl derivative

 $C_nH_1(NO_2)(OMe)(OH)CO_2H[x 3 4 1]$ Formed by boiling its acetyl derivative [182°] which is produced by the nitration of acetyl vanillic acid C.H. (OMe) (OAc) CO.H (Tiemann & Matsmoto, B 9, 945, 11, 132) Needles (from alcohol)

The isomeric C₀H₂(NO)(OMe)(OH) CO₀H [5 3 4 1] [202°] is formed by oxidation of acetyl nitro eugenol (Weselsky a Benedikt, M 3,

392), and crystallises in yellow needles

Methyl dermative $C_6H_2(NO)(OMe)(OH)CO_2H[6431]$ Formed from its acetyl derivative [169°], which is got by nitrating acetyl isovanillic acid (T a Needles

Dimethyl derivative CoHoNO C.H. (NO2) (OMe) CO2H Formed by nitration of veratric acid C6H3(OMe)2CO2H (T a M , Merch, Yellow needles (containing aq) A 108, 59)

Yields the ethers MeA' [144°] and EtA' [100°] Iso-nitro-protocatechuic acid Ds-methyl ether C₆H₂(NO₂)(OMe)₂CO₂H [202°] Formed by methylation of nitro-vanillic acid (T a M) Needles Yields MeA' [128°] crystallising in

Nitro protocatechuic acid Methyl-propyl ether O₁₁H₁₈NO₆: e C₆H₂(NO₂)(OMe)(OPr)CO.H Formed by nitration (Cahours, Bl [2] 29, 270)

Nitro-protocatechnic acid Mothylene ether CH2O, C.H4(NO)CO,H. [172°]. Formed 51) Got also from C.H4(NO)O.CH.CH(NO) by

from piperonylic acid CH₂<0>C₀H₂.CO₂H by nitration (Jobst a Hesse, B 11, 1031, A 199, 70) Needles -- KA' aq -PbA', aq -CuA,' 4aq. -AgA' needles or plates

NITROPRUSSIDES v vol 11 p 340

NITROPYROCATECHIN C.H.NO. & e C.H.NO. (OH).[4 2 1] [170°] Formed by the action of nitrous acid on pyrocatechin (Benedikt, B 11, 362, J pr [2] 18, 455) Formed also by boiling the carbonyl derivative of (5,2,1) nitro amido phenol with potash (Von Chelmicki, J pr [2] 42, 442) Small yellow needles (from ether) Its aqueous solution is turned purple by **a**lkalıs Dyes stuff mordanted with alumina orange (Kostanecki, B 22, 1347) -BaA" 3aq dark red plates, with metallic lustre

An isomeric nitropyrocatechin [86°] formed, together with the preceding, by nitra tion of pyrocatechin (Weselsky a. Benedikt, M 3, 386) A di methyl derivative of nitro pyrocatechin C₆H₃(NO₂)(OMe), [96°] is formed by nitrating veratrole (Merck, A 108, 60, Tie mann a Matsmoto, B 9, 939, 11, 131)

The methylene derivative

 $C_6H_v(NO_2)$ CO CH [148°] is a product of the action of nitric acid on piperonylic acid (Hesse, A 199, 73, 341) It crystallises in needles

Di nitro pyrocatechin $C_6H_2(NO_2)_2(OH)_2$ Methyl derivative C,H2(NO2)2(OMe)(OH) Di nitro guaracol [123°] Made by the action of nitrous acid gas upon an ethereal solution of guaracol at 0° (Herzig, M 3, 825) Plates The di methyl derivative C.H. (NO2)2 (OMe), formed by nitration of veratrol, melts above 100° (M) The methylene derivative C₈H₂(NO) O₁CH, [101°] is formed in the nitra tion of piperonylic acid (H)

Tri nitro-pyrocatechin Di methyl-deri

vative C₂H(NO₂)₃(OMe)₂. [145°] Got by minating C₃H₃(NO₂)(OMe)₂ (T a M) Prisms

DI NITRO-PYROCOLL C₁₀H₄(NO₂)₂N₂O₂ Got by mitrating pyrocoll (Ciamician a Danesi, G 12, 39) Yellow crystals, decomposing before

NITRO - PYROGALLOL $C_6H_2(NO_2)(OH)_3$ [205°] Got by passing nitrous fumes into an ethereal solution of pyrogallol (Barth, M 1, 882) Triclinic olive brown prisms (containing aq), a b c = 2 812 1 498 C.H (NO.)(OEt).2(OH) [123°] and C_eH (NO)(OEt)(OH)₂ [139°] are formed in the same way (Weselsky a Benedikt, M 2, 214) The compounds C, H(NO,) (OEt), [73°] and C.(NO.),(OEt), [93°] are formed by nitration NITROPYROMECONIC ACID C₂H₂(NO₂)O₃

Formed by nitrating pyromeconic acid (Ost, \vec{J} pr [2] 19, 192) Crystals (from alcohol) -NaA'-AgA

DI NITRO PYROMELLITIC ACID

C₆(NO₂)₂(CO₂H)₄[5 2 6 4 3 1] Formed by oxida tion of di nitro ψ cuminic acid $C_cMe_2(NO_d)_2CO_2H$ [205°] (Nef, C J 53, 428, A 258, 317) Long silky needles —Ag.A" amorphous pp

Methylether Me, A'v [180 6°]

Ethylether Et.Aiv [130°]
NITRO-PYROMUCIC ACID C.H.NO. 46. C₄H₂(NO₂)O CO₂H [184°] Formed from dehydromucic acid (1 pt), HNO₃ (10 pts), and cone H₂SO₄ (1 pt) (Klinkhardt, J pr [2] 25,

exidation with CrO₃ (Priebs, B 18, 1362) Yellow plates (from water) Yields succinic acid (and not an amido- acid) on reduction with tin and HClAq —CaA'2 —PbA'2 —AgA' Ethyl ether EtA' [1019

[101°]

DI-NITRO-PYRROLE C,H,(NO,),NH [152°] Formed by the action of fuming HNO, on pyrryl methyl ketone Formed also, together with an isomeride [173°], by the action of fuming HNO, on pyrrole carboxylic acid at 0° (Ciamician a Silber, B 18, 1462, 19, 1081, G 16, 347) Colourless plates BaA', yellow needles

NITRO PYRROLE CARBOXYLIC ACID C₄H₂(NO₂)NH(CO₂H) [217°] Formed by saponifying its methyl ether, which is got by mitrating C.H.NH(CO.Me) (Anderlin, B 22, 2505, Rend Accad Linc [5] 1, 40) Yellow needles (containing aq), sl sol cold water

Methyl ether MeA' [197°]
An isomeric acid [161°] may be obtained from its methyl ether [179°] which accompanies the preceding ether C₄H(NO₂)₂NH(CO₂Me)[115°] is also formed in the nitration

Nitro-pyrrole carboxylic acid [146°] Formed by boiling di nitro pyrocoll with potash solution (Ciamician a Danesi, G 12, 40) Minute needles (containing aq)—NH,A' prisms or

NITRO PYRRYLENE-DI-METHYL DIKE **TONE** $C_0H_0N_2O_4$ te $C_4H_2(NO_2)N(CO~CH_3)_2$ [149°] Formed by intrating pyrrylene di methyl di ketone (Ciamician a Silber, G 16, 347, B 18, 1467, 19, 1078) Needles (from water)

NITRO PYRRYL METHYL KETONE Bv

 $_{\rm nitrating\ NH} < \stackrel{\rm CH}{<_{\rm CAc\ CH}} \stackrel{\rm CH}{<_{\rm CH}}$ two compounds are formed [197°] and [156°] Both yield pps of $C_6H_5N_2O_9Ag$ (Ciamician a Silber, B 18, 413, 1457) A compound C₄H₂(NO₂)₂N CO CH₃ [114°] crystallising in yellow needles (containing aq) may also be obtained

(B 1) NITRO QUINOLINE C.H. N.O. 18 CH C(NO₂) C CH CH CH CH—C N CH Formed, together with the (B 4) isomeride, by the nitration of quinoline, especially in presence of fuming H_2SO_4 in the cold (Claus a Kramer, B 18, 1243, Noelting a Trautmann, B 23, 8654) Colourless needles (containing aq)

(B 2) Nitro-quinoline NO₂C CH C CH CH CH CH [150°] (La Coste, B 16, 669), [164°] (C a K) Formed by boiling p nitro aniline (25 pts), gly cerin (60 pts), nitro benzene (15 pts), and H₂SO₄ (50 pts) for 4 hours Needles (contain ing aq) -B'2H2PtCl, small yellow needles

Methylo-rodide B'Mel Needles (B 3)-Nitro-quinoline NO2 C CH C N CH CH CH C CH CH [131 5°] Formed from m nitro aniline, picric acid, glycerin, and H₂SO₄ (Claus a Stiebel, B 20, 3095) Needles—B'HCl [225°]—B'HNO₈

-B',H,PtCl, prisms

(B 4)-Nitro-quinoline CH CH——C CH CH CH C(NO₂) C N CH [89°] Formed by nitrating quinoline, and also by boiling o nitro-aniline with glycerin, nitro-benzene, and H.SO₄ (Königs, B 12, 449, La Coste, B 16, 678, Claus, B 18, 1243, Noelting, B 23, 3654) Formed also by heating quinoline (B 4)-sulphonic acid with HNO. (Claus a.

B 19, 2886), and by warming Kuttner, CaHa(NO2)(OMe) CH CH CHO with alcoholic ammonia (Miller a Kinkelin, B 22, 1716)
Prisms —B'₂H₄PtCl₆ orange needles
(B 2, 4) Di-nitro quinoline

C(NO,) CH'C CH CH [150°] Formed by CH C(NO₂) C N CH heating (4, 2, 1) di nitro aniline with glycerip, nitro benzene, and H2SO4 (La Coste, B 15, 562) Long slender needles

By the nitration of quinoline two isomeric di nitro-quinolines [183°] and [134°] may be got (Claus a Kramer, B 18, 1243) Their platino chlorides B'H H.PtCl, form yellow crystals

NITRO-QUINOLINE $(Py \ 3)$ CARBOXYLIC ACID C₉H₃(NO₂)(CO₂H)N [220°] Formed by boiling (Py 3) methyl quinoline (quinaldine) with nitric acid (S G 14) (Doebner a Miller, B 15, 3076) Crystals, sl sol cold water —AgA

NITRO RESORCIN $C_6H_3(NO_2)(OH)_2[4 + 1]$ [115°] Formed together with a volatile (2, 3, 1) isomeride [85°], in the preparation of diazoresorein by the action of nitious acid on an ethereal solution of resorcin (Weselsky, A 164, 1, M 1, 887) Lemon yellow needles When heated with concentrated sulphuric acid it yields $O(C_0H_3(NO_2)OH)$, (Hazura, M 4, 610, 5, 188) which forms Ba(C12H2N2O2) 2aq and b, 186) which forms $\mathrm{Ba(C_{1,11},N_{1},N_{2},0,7)}$ and $\mathrm{BaC_{1,2}H_{6}N_{2}O,5^{1}_{3}aq}$ The isomeride [85°] is converted by the action of nitrous acid into $\mathrm{C_{6}H_{2}(OH)O(NOH)(NO_{2})[1\ 3\ 4\ 2]}$ (De la Harpe a Reverdin, Bl [2] 49, 760) — $\mathrm{BaH_{2}A''_{2}5aq}$ — $\mathrm{BaH_{2}A''_{2}aq}$ — $\mathrm{BaH_{4}A''_{3}aq}$ golden needles

Methylethers $C_6H_3(NO_2)(OH)(OMe)[4\ 3\ 1]$ [95°] steam — $C_0H_3(NO)(OMe)(OH)[431]$ with Not volatile with steam

Ethyl ethers C_eH₃(NO)(OEt)(OH) [79°]

Volatile with steam [131°] Non volatile

Di acetyl derivative C, H, (NO) (OAc),
[91°] Tables (from alcohol) (Errera, G 15, 273)

Di benzoyl derivative $\mathbf{C}_6\mathbf{H}_3(\mathbf{NO}_2)(\mathbf{OBz})$ [111°] Got by nitrition (Schiaparelli a Abelli, G 13, 257, Errera, G. 15, 271)

Di m nitro-di benzoyl [123°]

Di nitro resorcin $C_0H_1(NO_2)_2(OH)$ [4 2 3 1] [142°] Formed by the action of nitrous fumes, or of cold HNO3, upon di nitroso resoicin (Benedikt a Hubl, M 2, 323, Barr, B 21, 1514, Von Kostanecki, B 21, 3122) Formed also by boiling di nitro m amido phenol with dilute KOHAq (Lippmann a Fleissner, M 6, 814, 7, 98) Golden leaflets $-K_2A''$ aq -BaA'' — Ag₂A" red pp

Methylthy l ether $C_8H_2(NO_2)_2(OMe)(OH)$ Needles (Aronheim, B 12, 30)

Di nitro resorcin C₆H₂(NO₂)₂(OH)₂ Formed by nitration of the di acetyl derivative of resorcin (Typke, B 16,552) Yellow prisms or needles —(NH₄)₂A'' —BaH₄A''₂—BaA'' red scales with violet lustre, v sl sol water

 $Ethers C_6H_2(NO_2)_2(OMe)_2$ [67°], $C_6H_2(NO_2)_2(OEt)_2$ [75°] Obtained by nitra tion of the ethers of resorein (Honig, B 11,

1039 , Aronheim, B 12, 82)
Tri nitro resorcin C₆H(NO₂)₂(OH)₂-[6 4 2 3 1] Oxypicric acid Mol w 245 Styphnic acid[175]. 8. at 14° (Stenhouse, Pv. 19, 410).

Formation —1 By the action of boiling nitric acid on extract of Brazil wood, or sapan wood, suxanthone, gum ammoniac, asafætida, galbanum, peucedanin, ostruthin, saganenum, or the aqueous extract of fustic or sandal wood (Chevreul, A Ch 66, 116, 73, 48, Erdmann, J pr 37,409, 38, 355, Bottger a Will, A 58, 273; Rothe, J pr 46, 376, Gorup Besanez, A 183, 336, Stenhouse, C J 19, 236) Graebe, B 22, 1405) -2 By the action of nitric acid on m-nitro phenol, on γ , δ , or ϵ di nitro phenols, and on β or γ tri nitrophenol (Bantlin, B 10, 524, 11, 210), Henriques, A 215, 340) -3 By the nitration of resorcin or of either di nitroresorcin (Merz a Zetter, B 12, 681, Benedikt a Hubl, M 2, 326, Von Kostanecki, B 21, 3122) By boiling tri nitro phenylene di methyl diamine with potash (Romburgh, R T C 7, 6) -5 Together with three di nitro benzoic acids, by adding o nitro benzoic acid to a mixture of fuming HNO, and H₂SO, (Griess, B 7, 1224, Salkowski, B 8, 637)

Properties - Yellow lamine Ppd from its aqueous solution by HCl V sol alcohol and

Salts — $(NH_4)HA''$ — $(NH_4)_2A''$ monoclinic needles, $a b \iota = 1 \ 1 \ 66 \ 2 \ 0'$, $\beta = 70^{\circ} \ 52'$ — $Na_3A'' \ 2\frac{1}{2}aq$ — KHA''aq — KA'' — $BaA'' \ 3aq$ — BaA"aq - SrA' 2aq CaA" 3½aq Pb (OH) A" MRIA" 12aq - CoA" 33aq - CaK A', 4aq - NıK.A" 3aq - CuA" 4aq - Cu(NH₁).A"₂7aq - CuK.A", 4aq - Ag.A"aq slender needles

Methyl ether Me A" [124"] Formed by

Stretting CH (M), (Mong R. 11, 1330)

nitrating C,H₁(OMe), (Honig, B 11, 1039)

Diethylether EtA" [121°] Yields
trinitro m phenylene diamine on heating with ammonia (Nolting a Collin, B 17, 259)

NITRO RESORCIN SULPHONIC ACID ${
m C_6H_2(NO)(OH)_2(SO_3H)}$ [124°] Formed by sulphonating nitro resorcin [115°] (Hazura, M4, 610) Minute crystals (containing 1 aq) -BaA''', 4aq yellow needles - BaA''' 2aq yel low scales -- Ba,A,"'' 10aq blood rcd needles

A nitro resorcin disulphonic acid is formed by oxidising the corresponding nitroso compound with HO, (Ulzer, M 9, 1130)

ACÍD 🕏 NITRO SALICYLIC NITRO-OXY BFNZOIC ACID

NITROSAMINES Compounds containing nitrosyl (NO) united to nitrogen scribed under the amines from which they are derived by displacement of hydrogen by nitrosyl Nitrosamines are formed by the action of nitrous acid upon secondary bases. They are neutral substances and may be reconverted into the parent base by boiling with tin and HClAq, with zinc and H2SO4, with aniline, or with alcoholic potash (Geuther, A 128, 151, Griess, E 7, 218, Witt, C J 33, 203) Many aromatic nitros amines are converted into p nitroso compounds by alcoholic HCl, the nitrosyl entering the benzene nucleus (Fischer a. Hepp, B 20, 1247,

This name is given by Wal NITROSATES lach (A 241, 288) to compounds formed by the union of nitrogen peroxide with unsaturated hydrocarbons Thus Guthrie's 'amylene nitrite' (vol 1 p 210) would be called amylene nitrosate and may be represented as nitrosoamyl nitrate of formula C₅H₁₀(NO)(O NO₂) or D.H. (NOH) (ONO.) This body reacts with aro-

matic bases forming C,H,(NOH)NPhH [141°], C.H. (NOH)NHC.H. Me[1 4] [112°], and the isomeric C.H. (NOH)NHC.H. Me[1 2] [115°], which yield nitrosamines melting at 128°, 148°, and 150° respectively Amylene 'nitrosate' reacts in like manner with o anisidine, piperidine, and diethylamine, forming bases melting at 139°, 96°, and 72° respectively These bases are termed introl amines by Wallach

The term nitrosite is given by Wallach to compounds resulting from the union of N2Os with unsaturated hydrocarbons Thus terpinene nitrosite $C_{10}H_{18}N_2O_3$ may be viewed as a nitroso nitrite with formula $C_{10}H_{16}(NO)(ONO)$ or $C_{10}H_{15}(NOH)(ONO)$ They readily exchange O NO for NHR' or NR'R" when acted upon by bases, forming nitrolamines Thus terpinene nitrosite acted upon by ethylamine yields 'terpinene nitrol-ethylamine ' C, H, (NOH) NHEt [131°

NÍTROSO ACETIC ETHER v OXIMIDO ACETIC ETHER

NITROSO ACETOACETIC ETHER C.H.NO. se CH, CO C(NOH) CO2Et [54°] Formed by the action of nitrous acid on aceto acetic ether, and on acetyl malonic ether (V Meyer a Züblin. B 11,320, Wleugel, B 15,1050, Ceresole, B 15, 1326, Lang, B 20, 1327) Prisms, sl sol water, sol alkalis Forms CH, C(NOH) C(NOH) CO,Et.

Anilade CloHisNO. [100°] Formed by the action of nitrous soid on the anilade of acetoacetic acid (Knorr, A 236, 80) Prisms NITROSO TRIACETONAMINE 9. ACETOM-

AMINE

NITROSO ACETONE C.H.NO. i.e. CH, CO CH NOH or CH, CO CH, NO of pyruvic aldehyde Oxim of methyl glyoxal. [65°] Formed by the action of nitrous acid on acetoacetic ether (V Meyer a Zublin, B 11, 695, Ceresole, L 15, 1326), and by warming acctone with amyl nitrite and HCl (Claisen, B 20, 252) Silvery leaflets or prisms, boiling with decomposition at about 200° V sol water and May be sublimed alcohol, volatile with steam

Reactions -1 Dilute HClAq at 140' forms acetic and formic acids and ammonia (Treadwell and Steiger, B 15, 1059) -2 Tin and HCl give di methyl pyrazine.—8 Hydroxylamine hydrochloruse forms methyl glyoxim or acetoxminc acid (vol 1 p 38) and a compound, C,H,N,O,, which detonates at 238°-247°, and forms an explosive hydrochloride C,H,N,O,HCI [113°] (Scholl, B 23, 3578) — 4 Phenyl hydrasine yields CH, C(N,HPh) CH NOH [134°] (Pechmann, B 21, 2994) — 5 Phenyl methyl-hydrasine yields CH, C(N MePh) CH NOH [118]

Methylether C, H, O(NOMe) (115° uncor) Formed by heating nitroso acetone with NaOMe (Meyer a Ceresole, B 15, 8067, 16, 833) Colourless oil

Benzyl ether C,H,O(NOEt) (130°),
Benzyl ether C,H,O(NOC,H,) [40]

Di-nitroso-acetone CH(NOH) CO CH(NOH). [144°] Formed by the action of nitrous acid on acetone dicarboxylic acid (Pechmann a. Wehsarg, B 19, 2465, 21, 2992) Prisms, sl. sol cold water, decomposed by boiling water into HCy, CO2, and water Explodes when heated

Phenyl hydraside N.HPh C(CH NOH).
[145] Needles. Yields a mono-acetyl deriva-

Phenyl - methyl - hydrazide [137°] Crystals

Oxim CH(NOH) C(NOH)CH(NOH)

ntroso propane [171°] Crystalline powder NITROSO-ACETOPHENONE C.H.,NO. 1 e C.H. CO CH NOH Oxim of phenyl glyoxylu al dehyde [128°] Prepared by the action of amyl nitrite and NaOEt on acetophenone (Claisen a Manasse, B 20, 2194, Braun, B 22, 556) Thin, monoclinic plates, abc = 276212146, $\beta = 66^{\circ}$ 54' Sl sol cold water, soluble in aqueous Na,CO, On heating with Ac O it yields C.H. CO CN SnCl, in HClAq, reduces it to ω amido acetophenone and di phenyl pyr When its compound with NaHSO, is boiled with H₂SO₄ it yields C₆H₅ CO CHO Hy droxylamine hydrochloride yields C₁₆H₁₃N₃O₃ [207°-211°] (Scholl, B 23, 3580)

Oxim v Oxim of PHENYL GLYONAL

p NITROSO-ANILINE C₆H₄(NO)(NH)[14] [174°] Formed by heating nitroso phenol with NH,Cl, ammonium acetate, and ammonium carbonate (Fischer a Hepp, B 20, 2175, 21, 684) Steel blue needles (from benzene) composed by NaOHAq into NH3 and nitroso phenol Tin and HCl reduce it to phenylene p diamine Phenyl hydrazine hydrochloride forms $C_{12}H_{12}N_4O$ [125°] Phenyl methyl hydrazine yields $C_{13}H_{14}N_4O$ [151°] $-C_6H_5NaN_2O$ 2aq yel low crystals

NITROSO-ANTHRONE v ANTHRACENF

NITROSO-BENZENE *C.H. NO On distil ling with steam, the product of the action of nitrosyl chloride on HgPh2, there is obtained a pungent green liquid, which yields aniline on reduction (Baeyer, B 7, 1638). By oxidising the di-oxim of quinone with alkaline KaFeCy, there is obtained a golden yellow pp, probably di nitroso benzene $C_6H_4(NO)_2[1 \ 4]$ It yields p phenylene diamine on reduction, and p di nitro benzene on warming with HNO, Hydroxyl amine hydrochloride converts it into quinone dioxim

NITROSO - BENZYL ALLYL - THIO UREA PhC(NOH) NH CS NHC₃H₅ Formed by melting together allyl thiocarbimide and benzamidoxim (Koch, B 24, 899) Fine needles

ISO-NITROSO-BENZYL-AMINE BENZ ENYL AMIDOXIM

p NITROSO-DI-BENZYL-ANILINE

 $C_6\tilde{H}_4(NO) N(CH_2 C_6H_5)_2$ [92°] Formed by adding amyl nitrite to a solution of di benzyl aniline in alcoholic HCl Thin steel blue plates, or small green crystals V sol ether and CS₂, m. sol. alcohol On reduction it gives u di benzyl-p-phenylene diamine (Matzudaira, B 20,

NITROSO-BENZYL-MALONIC ACID

C,H, C(NO)(CO,H)₂. [120°] Obtained from its ether, which is got from nitroso malonic ether, NaOEt, and benzyl chloride (Conrad a Bischoff, On fusion, or A 204, 121, 209, 215) Plates on boiling with water, it gives benzyl alcohol, CO, and HCy—K, A" aq (dried at 100°) NITROSO - BENZYL TOLYL - THIO

PhC(NOH) NH CS NH C,H,Me [67°] Formed by melting p tolyl thio carbimide with benzamidoxim (Koch, B 24, 397)

C,H,NO, NITROSO - BETORCIN $C_6H(NO)Me_2(OH)_2[x 1 4 3 5]$ Obtained by the action of nitrosyl sulphate SO, H(NO) on a solu-

tion of betorein (Stenhouse a Groves, C J 87, 404, Von Kostanecki, B 19, 2323) Red prisms (from HOAc)

p NITROSO-ISOBUTYL-ANILINE

C₆H₄(NO) NHCH₂Pr [94°] Formed from 180 butyl aniline, NaNO₂, and HCl (Wacker, A 243, 297) Steel blue crystals, v sol alcohol C₆H₄(NH₂) NHCH₂Pr on reduction alkalis split it up into p nitroso phenol and iso butylamine Further treatment with NaNO, and HCl yields C6H4(NO) N(NO)CH2Pr

a NITROSO-n BUTTRIC ACID C,H,NO, te C,H, C(NOH) CO₂H [151°] Formed by the action of nitrous and and NaOH upon ethyl acetoacetic ether (Wleugel, B 15, 1057) Flat

prisms - AgA' insoluble powder

β Nitroso butyric acid CH₃ C(NOH) CH₂ CO₂H [140°] Obtained from its ether, which is got by the action of hydroxyl amine on acetoacetic ether (Westenberger, B 16,

2996) -AgA' white pp

(aβ) Di isonitroso butyric acid C4H6N2O4 i e CH, C(NOH) C(NOH) CO H Obtained from 1t4 ethyl ether [140°] which is formed, together with the anhydride C₈H₁₀N₄O, [133°], by the action of hydroxylamine on nitroso acetoacetic cther (Ceresole a Kockert, B 17, 821) The and 18 crystalline and gives the salts BaA', 2'aq and AgA' The anhydride gives BaA'' a and The anhydride gives BaA" and $\widetilde{Ag_2A''}$

NITROSO CARVACROL

 $C_6H_2(NO)(C_9H_7)(CH_9)(OH)$ [153°] Yellow prisms (Paterno a Canzoneri, B 12, 383 Reduced by SnCl₂ to amido carvacrol [304°]

NITROSO-CARVENE v CARVOXIM

NITROSO COMPOUNDS Compounds con taining nitrosyl NO They are usually obtained by the action of nitrous acid. They may be divided into nitrosamines (q v) in which nitrosvil is attached to nitrogen, and nitroso compounds proper in which nitrosyl is attached to carbon Compounds in which nitrosyl is attached to oxygen are called nitrites Compounds contain ing the divalent radicle oximidogen NOH are often called isonitroso compounds, the group C NOH being isomeric, and often interchinge able, with the group CH NO The isonitroso compounds may be obtained by the action of hydroxylamine on aldchydes, ketones, and hydroxylamine on aldehydes, ketones, and ketonic compounds, and may thus be termed oximides, oximes, or oxims of these ketonic Nitrous acid acting upon the group bodies CO CH₂ frequently converts it into CO C(NOH) the new body may be termed either a nitroso derivative of the original ketone, or a mono oxim of the diketone CO CO, the latter termi nology is that usually employed in this dic tionary Nitrous acid acting upon a secondary amine forms a nitrosamine, with tertiary aro matic amines and with phenols it yields nitroso compounds, the nitrosyl taking up the para position When the p position is occupied the nitrosyl can in some cases still enter the benzene nucleus in the o position The nitroso phenols HOC CH CH CON and the oxims of the

mono quinones CO CH CH CH C NOH are iden tical, and will be described under the quinones Some aromatic nitrosamines are converted into the isomeric p nitroso compounds by the action of alcoholic $\dot{\mathbf{H}}\mathbf{C}\mathbf{l}$

NITROSO-CREATININE v CREATININE

NITROSO-CRESOL v Oxim of TOLUQUINONE DI-NITROSO CRESORCIN C₆HMe(NO)₂(OH)₂ or C₆HMe(NOH)₂O₂[1 3 5 2 4] Formed from cresorcin and HNO₂ (Von Kostanecki, B 20, 3135) Pale green plates (containing aq) Explodes above 160° Sl sol water With HNO₂ it yields di nitro cresorcin [90°]

DI-NITROSO-CYMENE O₁₀H₁₂N₂O₂ [72°]. Formed by oxidising the dioxim of thymoquinone with alkaline K₂FeCy₅ (Kehrmann a Messinger, B 23, 3560) Greenish yellow pp, smelling like iodine After one fusion it melts

at 130°

NITROSO-ETHYL-ACETONE is the (β) oxim

of Methyl ethyl diretone $(q \ v)$

NITROSO-ETHYL-ANILIÑE C_eH₁₀N₂O • e [4 1]C_eH₄(NO)(NHEt) [78°] Obtained by adding alcoholic HCl to an ethereal solution of the nitrosumine of ethyl anilne (Fischer a Hepp, B 19, 2993) Green plates, v sol alcohol Yields C_eH₄(NH₂)(NHEt) (270°) on reduction On heating with aqueous NaOH it is split up into nitroso phenol and ethylamine —B'HCl needles, v sol water

Nitroso di ethyl aniline [1 4]C₀H₄(NO) NEt₂. [84°] Formed from di ethyl aniline and nitrous acid (Kopp, B 8, 621) Green prisms (from ether) Decomposed by boiling dilute NaOH into nitroso phonol and diethylamine Salts—B'2H.PtCl₃—B' I₃. [118 5°] (Dafert, M 4, 506)—B'₃I₂. [127°]—B H₂SO₄—B'2C₃H₂(NO₂)₃(OII)—B'HCy [171°] (Lippmann, M 6, 544) Oran₅e crystals (from alcohol)

NITROSO DI ETHYL KETONE v (a) Oxim of METHYL ETHYL DIKETONE

a NITROSO ETHYL-PHENYL AMINE

 $C_aH_1(NH_2)$ CH(NO) CH₃ Formed by heating $C_aH_1(NH_2)$ CH NO with KOH, methyl alcohol, and MeI at 100° (Gabriel a Meyer, B 14, 2339) Yellowish oil — B'HCl prisms

Acetyl derivative

C_bH₄(NHÃc) CH(NO) CH₄ [109°]

NITROSO ETHYL O TOLUIDINE C,H, NO to C,H,Me(NO) NHEt [140°] Green plates (bischer, B 19, 2994)

NITROSO ETHYI-o-XYLIDINE C, H, NO 1 e C, H, (NO)Me, (NHEt) [1 2 3 4] [124°] Green Clystals (Menton, A 263, 827) —B'HCl needles NITROSO FORMANILIDE v FORMIC ACID

a NITROSO GLUTARIC ACID

CO₂H C(NOH) CH₂CH₂ CO₂H [152°] Produced by boiling furazyl propronic acid

NCH NCH₂CH₂CO₂H [86°] with potash, the semi nitrile CN C(NOH) CH₂CH₂CO₂H [87°] being formed at the same time (Wolff, A 260, 112) Prisms Yields amido-glutaric acid on reduction—Bah"1½aq needles, v sl sol water

Amrdoxim
CO,H CH, CH, C(NOH) C(NOH) NH... [158°]
Formed by the action of hydroxylamine on the semi nitrile [87°] Needles, sl sol water

NITROSO GUANIDINE v GUANIDINE

NITROSO HEXOIC ETHER

OH, C(NOH) CHEt OO, Et Formed from ethylacetoacetic ether and hydroxylamine (Westenberger, B 16, 2997) Oil.

Nitrosc hexoic acid CH₁ C(NOH) CMe₂ CO₂H [97°] By the action of amyl intrite and intrice acid on tri methyl ethylene there is formed a compound CMe₂(ONO₂) C(NOH) CH₃, which when heated with alcoholic KCy yields the nitrile CH₄ C(NOH) CMe₂ CN [100°] (230°) which forms on saponification the corresponding amide [164°] and acid [97°] (Wallach, A 248, 166) The acid is split up by heat into CO₂ and the oxim of methyl isopropyl ketone

NITROSO-ÎNDOXYL v \(\psi \)-ISATIN OXIM
NITROSO MALONIC ACID OH(NO)(CO,H),
or C(NOH)(CO,H) Oxim of mesoxalic acid

or C(NOH)(CO,H) Oxim of mesozalic acid
Formation—1 By treating barbituric acid
with nitrous acid and warming the resulting
violuic acid with potash (Baeyer, A 131, 292)
2 From its ether, which is got by passing nitrous
fumes into sodium malonic ether (Conrad a
Bischoff, B 13, 599, A 209, 211)—3 By the
action of hydroxylamine on mesoxalic acid
(Meyer a Muller, B 16, 608)

Properties — Needles Decomposes at 126° with violence At 40° its aqueous solution gives off CO₂ and HCy Sodium amalgam reduces it

to amido malonic acid

Salts —K.A" laq —PbA" aq —AgA' laq Ethyl ether Et.A" SG lis 1149 Oil NITEOSO MESITYL OXIDE

CMe CH CO CH NOH [102°] Prisms (Claisen a Manasse, B 22, 526)

NITROSO METHYL ACETONE v Oxim of Di methyl diketone

needles

ether)

NITROSO DI METHYL p AMIDO BENZOIC ACID C₆H₂(NOH)(NMe₂) CO₂H [224°] Formed by the action of nitrous acid on C₆H₄(NMe₂)CO₂H (Bischoff, B 22, 342) Plates (from alcohol) Yields C₆H₄(NMe₂)CO₂H on reduction with SnCl₂ and HCl Salts -B'H C₂O₄ [178°-181°] - B'C₆H₂(NO₂)₈OH [168°] - B'HCl slender

Methyl ether MeA'6'aq [101°] —B'HCl -B'C,H₂(NO,),0H Golden yellow needles NITROSO DI METHYL - AMIDO BENZO

NITROSO DI METHYL AMIDO BENZO PHENONE C.H. CO C.H. (NOH) NMe. Oi (Bischoff, B 22, 340)

Nitroso-tetra-methyl-diamido-bensophenone v p 263

p NITROSO-METHYL ANILINE C, H₈N₂O t.e C₅H₄(NO) NMeH [118°] Formed by adding also holic HCl to an ethereal solution of the mitrosamine C₅H₄, NMe(NO) (Fischer a Hepp, B 19, 2991) Steel blue prisms (from water) Decomposed by NaOHAqinto p mitroso phenol and methylamine Yields C₆H₄(NH₂)(NMeH) on reduction Nitrous acid forms the nitrosamine C₆H₄(NO) NMe NO [101°] Nitric acid (S G 1 13) yields the nitrocompound C₆H₄(NO₂) NMe NO [104°]

Nitroso-di-methyl aniline C₆H₄(NO)NMe₂ or C₆H₄(NO)NMe₂ O Mol w 150 [85°] Formed by the action of nitrous acid on di-methyl aniline hydrochloride (Baeyer a Caro, B 7, 963, Schraube, B 8, 616, Wuister, B 12, 523, 1825, Meldola, C J 39, 37) Green plates (from

Reactions —1 Reduced by tin and HClAq to C_sH₄(NH₂)(NMe₂) —2 Resolved by boiling alkalinto nitroso phenol and dimethylamine — 8 K₄FeCy₆ oxidises it to C₅H₄(NO₂)(NMe₂).

4 Alcoholic potash forms NO(C₂H₃NMe₂).

5 HClAq at 105° yields C₆H₄(NH₂)(NMe₂).

C₄H₂Cl₂(NH₂)(NMe₂) and C₄H₂Cl₂(NH₂)₂ (Möhlau, B 19, 2010) — 6 Phenyl hydrazine acetate yields C₁₄H₁₆N₄O [108°] This base is also yields C₁₄H₁₆N₄O [103°] formed by the action of diazobenzene on nitroso dimethylaniline (O Fischer, B. 21, 2610, 22, 623) Phenyl methyl hydrazine yields the com nound C18H18N4O [141°]

Salts -B'H₂C₁Q [121]
Salts -B'HCl yellow needles -B'H₂CO₄
-B'H₂C₂O₄ 2aq -B'H₂C₂O₄ -B'₂H₄FeCy₆ aq
-B',H₄FeCy₆2½aq -B'₂AgNO₃ -B'₂HOy [222°]
(Lippmann a Fleissner, M 6, 537)

Combinations —B'I₃ [116°] (Dafert, M 4, 506) —B'₂I₂ [124°] —B'₂PhNH₂ steel blue crystals —B'₂NH₂ C₆H₄Me [1 4] —B'₂PhOH — B'C₂H₄ dark green crystals —B'₂HCyC₆H₄— [116°] (Dafert, M B',HCyC,H,NO,

B',HCyO,H, — (B',HCy),(PhN2),
NITROSO-METHYL OXINDOLE v. Oxim of

METHYL-ISATIN

NITROSO-METHYL-o-TOLUIDINE

C_eH₂Me(NO)(NHMe) [1 5 2] Formed [151°] by the action of HCl on the isomeric nitros amine C_sH₄Me(NMe NO) (Kock, A 243, 308) Green plates Split up by boiling NaOHAq into nitroso-o cresol and methylamine KMnO₄ oxidises it to nitro methyl o toluidine —B'H₂Cl₂ aq [110°] Yellow cubes

Nitroso di-methyl m-toluidine

 $C_6H_3Me(NO)NMe_2[1\ 2\ 5]$ [92°] Formed by the action of nitrous acid on di methyl m toluidine (Wurster a Riedel, B 12, 1796, 13, Light green needles Decomposed by boiling NaOHAq into NMe, H and the oxim of m toluquinone —B'HCl —B',H,FeCy, aq -B',H,FeCy, 2aq yellow needles NITROSO-METHYL-o-XYLIDINE

C₆H₂Me₂(NO)(NHMe) [1 2 6 3] [161°] Green needles, sl sol water (Menton, A 263, 323) B'HCl crystalline meal

NITROSO-NAPHTHALENE C₁₀H₇(NO) [89°] Formed from Hg(C₁₀H₇)₂ and NOBr in CS₂ (Baeyer, B 7, 1639, 8, 615) Yellow crystals

Di-nitroso-naphthalene C₁₀H₆(NO)₂[14] Formed by the action of alkaline K. FeCy, on the dioxim of (a)-naphthoquinone (Nietzki a Guiter mann, B 21, 433). Pale yellow powder, exploding at 120° Insol water and alcohol

Di-nitroso naphthalene C₁₀H₆(NO)₂[1 2] [126°] Formed from (\$\beta\$) naphthoguinone dioxim and K.FeCy. (Leuckart, B 19, 174) Needles,

m sol alcohol

NITROSO-NAPHTHOL v Oxim of Naphtho

NITROSO (β) NAPHTHOLSULPHONICACID $C_{10}H_s(NO)(OH)SO_sH$ or $C_{10}H_s(NOH)O(SO_sH)$ [1 2 3] or [1 3 2] Formed from ammonium (β) naphthol sulphonate, NaNO2, and HCl (Meldola, C J 39, 41) Very soluble orange crystals solution gives with phenol in HOAc a blue colour, becoming red on dilution, and with diphenyl amine a blue colour, remaining blue on dilution Tin and HCl reduce it to the amido acid-BaA'2 aq orange needles -BaC10H5NSO, 2aq green needles — $Ag(NH_4)A'' - (NH_4)_2A''$ aq green -MgA"3aq orange -ZnA"3aq -PbA"aq

An isomeric acid, obtained by reducing benz ene azo (8) naphthol sulphonic acid with aque ous ammonium sulphide, crystallises in sparingly

soluble grey needles (Griess, B 14, 2042) NIΓROSO-DI-(α) NAPHTHYL-AMINE C₁₀H₀(NO) NHC₁₀H₇. [169°] Formed from

(C₁₀H₁)₂N NO and alcoholic HCl (Fischer a. Hepp, B 20, 1248, Wacker, A 243, 301) Dark red needles With boiling dilute H₂SO₂ it yields the mono oxim of (a) naphthoquinone and (a) naphthylamine—B'HCl green needles Nitroso (β) naphthylamine

 $C_{10}H_{c}(NO)NH_{2}[1\ 2]$ [152°] Formed by heating the (a) exim of (3) naphthoquinone with NH, Cl and NH, OAc (Ilinski, B 17, 391, Harden, A 255, 150) Dark green needles (from dilute alcohol Yields naphthylene o diamine on reduc tion and the di oxim of (3) naphthoquinone on treatment with hydroxylami...e - B'HCL --B'2H2PtCl -B'H2SO aq

NITROSO - (β) - NAPHTHYL-ETHYL -AMINE C₁₀H₆(NO) NHEt [121°] Formed by the action of alcoholic HCl at 6° on the nitros imine C₁₀H, NEt(NO), and also by the action of ethyl amine on the (a) oxim of (β) naphthoquinone (Fischer a Hepp, B 20, 2471, 21, 686) Green crystals Yields a crystalline nitrosamme C₁₂H₁₁N₂O₂, decomposing at 105°

(a) Nitroso-(a) naphthyl ethyl amine $C_{11}\dot{H}_{12}N_{2}O$ is $C_{10}\dot{H}_{4}(NO)NHEt[1\ 1]$ [133°] Formed in like manner (Kock, A 243, 310) Brown pp Reduc C₁₀H₆(NH)(NHEt) Reduced by stannous chloride to Yields ethylamine and C10H6(NOH)O when boiled with NaOHAq -BHČI — Picrate C18H15N,O8 [174°] · C₁₂H₁₃N₂O₂Na white spangles, v sol water

Tetrahydride C₆H₈ C(NHEt) CH C(NO) = CH

[119°] Formed from the isomeric nitrosamine and alcoholic HCl (Bamberger a Helwig B 22, 1314) Needles —B'HCl golden crystals Nitroso naphthyl di ethyl amine C₁₀H₆(NO) NEt₂ [165°] Formed by adding NaNO, to a well cooled solution of the base (B E Smith, C J 41, 182) Reddish golden scales Gives a blue colour with H₂SO

NITROSO-NITRATES v NITROSATES

NITROSO-NITRO ANTHRONE C,H,N,O, [263°] Formed by the action of alkalis on hydro anthracene nitrite (Liebermann, B 14, 467, cf vol 1 p 277)

NITROSO-NITRO-BUTANE C,H,N2O, CH, C(NO)(NO₂) C₂H₄ PseudobutyInstrole [58] Formed by the action of KOH, KNO, and dilute $\mathbf{H}_2\mathbf{SO}_4$ on β nitro butane (Meyer a Locher, A 180, 136) and of NO on $\mathbf{CH}_1\mathbf{C}(\mathbf{NOH})\mathbf{C}_1\mathbf{H}$, (Scholl, B 21, 508) White prisms (from chlo roform), yields a blue liquid on fusion water and alkalıs

Pr CH(NO)(NO2) isomeric The and PrCH(NO)(NO₂) are oils (Demole, B 7, 790, Züblin, B 10, 2084)

NITROSO NITRO PENTANE Et, C(NO) (NO,) [68°] Formed from Et, C NOH and N.O. (Scholl, B 21, 509)

NITROSO-NITRO-PROPANE C.H. N.O. + e CH, C(NO)(NO₂) CH, [76°] Formed acetoxim and N₂O₄ (Scholl, B 21, 508) Formed from The isomeric compound CH, CH, CH, CH(NO)NO, or CH, CH₂ C(NOH) NO₂ melts at 60° (Meyer, A 175, 114)

NITROSO-NITRO RESORCIN C.H.N.O. . c. C₆H₂(OH)(NO₂)O(NOH) [1 2 3 4] Formed from nitro resorcin [85°] and nitrous acid (De la Harpe a Reverdin, B 21, 1405) Brown needles, not melted at 200°, explodes at a higher temperature.

NITROSO ORGIN C.H.2Me(NO)(OH), Formed from orom, NaOHAq, and amyl nitrite (Kramer, B 17, 1886) Dark red prisms When heated with orein and H₂SO₄ it gives the dyestuff C₁₄H¹₁₁NO₈

Di nitroso orcin C₆HMe(NO)₂(OH)₂[1 2 4 3 5] Formed by adding H SO, containing N2O3 to a solution of orcin (Stenhouse a Groves, C J 31, Yellow prisms Blackens about 140° without melting Alcoholic hydroxylamine hydrochloride at 100° yields C₀HMe(NOH),, whence Ac,O torms C₀HMe(N₂O), [47°) (Goldschmidt, B 20, 1607) The compound C. HMe(NOH), yields, on oxidation by potassium ferricyanide, the product CoHMe(NO), [103°], orystallising in paleyellow needles

NITROSO OXANTHRANOL C, H, NO, Formed by boiling 'hydro anthracene nitrite with alkalis (Liebermann, B 14, 471) Orange flakes, sol alkalıs

NITROSO OXINDOLE v ISATIN OXIM NITROSO OXY METHYL QUINOLINES

C₅H,N C₄HMe(NO)(OH) The following crystalline compounds have been obtained by the action of nitrous acid on the oxy methyl quinolines (Noelting a Trautmann, B 23, 3665) (B 3) nitroso (B 4) oxy (B 1) methyl quinoline, (B 1) nitroso (B 4) oxy (B 2) methyl quinoline, (B 4) nitroso (B 1) oxy (B 2) methyl quinoline, (B 1) nitroso (B 4) oxy (L 3) methyl quinoline, and (B 2) nitro-o (B 1) oxy (B 4) methyl quin Friedlander and Muller (B 20, 2011) have obtained in like manner (Py 1,3) nitrosooxy (Py 4) methyl quinoline crystallising in red

NITROSO OXY DI PHENYL AMINE

C₆H₃(NO)(OH) NHPh [4 3 1] Formed from C, H, (OH) NPh(NO) and alcoholic HCl (Kohler, B 21, 909) Red needles, m sol alcohol

NITROSO (B 4) OXY QUINOLINE

C,H,(NO)(OH)N Formed from o oxy quinoline and nitrous acid (Lippmann a Fleis mei, M 10, The reomeric nitroso 794) Yellow needles (B 2) oxy quinoline crystallises from HO to in golden needles (Matheus, B 21, 1886)

(Py 2) Nitroso (Py 1,3) di oxy quinoline

C.H. CO C(NOH) [208°] Formed by the action of nitrous acid on (Py 1,3) di ovy quinoline (oxycarbostyril (Baeyer a Homolka, B 16, 2216) Orange prisms Decomposed by cone HClAq into isatin and hydroxylamine yields tri oxy quinoline

NITROSO PHENOL v Mono-oxim of Quinone NITROSO PHENYL ACETIC ACID v Oxim of Phenyl Glyoxylic acid

p NITROSO DI PHENYL-AMINE

C.H.(NO) NPhH [143°] Formed from diphenyl nitrosamine and alcoholic HCl (O Fischer a Hepp, B 19, 2991, 21, 677, 2614) Green plates (from benzene) With phenyl hydrazine hydrochloride it yields a compound CisHieN.O Free phenyl hydrazine in ether yields a mido diphenylamine [75°] and $C_{20}H_{20}N_{1}O$ [173°] p Bromo aniline yields $C_{10}H_{20}R_{1}N_{1}$ [243°] Tin and HOI reduce it to $C_{10}H_{10}(N_{10}N_{10})$ (Ikuta, A 243, 274). Aqueous NaOH yields aniline and quinone oxim. -B'HCl bronze tables or needles

Acetyl derivative [97°] Red prisms Netrosamene C.H. (NO).NPh(NO) [98°].

NITROSO-PHENYL BENZYL-THIO-UREA PhC(NOH) NH CS NHPh [172°] Crystals (from

alcohol) (Koch, B 24, 394)

NITROSO-PHENYL (a)-NAPHTHYL AMINE

C₁₀H_c(NO) NHPh [150°] Formed from phenylnaphthyl nitrosamine and alcoholic HCl (Fischer a Hepp, B 20, 1247) Brownish yellow crystals Yields C₁₀H₆(NH₂) NHPh on reduction Boiling dilute H₂SO₄ splits it up into aniline and quinone oxim—B'HCl green plates

TRI NITROSO PHLOROGLUCIN C₆(NO)₃(OH)₃ Prepared by the action of KNO. and HOAc on phloroglucin (Benedikt, B 11, 1374) Needles, sol water and alcohol —K.A"" needles, exploding above 130°

TRI-NITROSO-PROPANE . Oxum of Dr-

NITROSO ACETONE

NITROSO PROPIONIC ACID v. Oxim of PYRUVIC ACID

NITROSO PROPYL-ANILINE C,H12N2O 16 C₆H₄(NO) NPrH [59°] Formed from the 180 meric CoH, NPr(NO) and alcoholic HCl (Wacker, A 243, 291) Steel blue needles, v sol alcohol Yields C.H.(NH.) NPrH on reduction, and quinone oxim and NPrH2 on boiling with alkalis NaNO₂ and HCl yield C₆H₄(NO) NPr(NO) [69°]

Nitroso di propyl-aniline CeH4(NO) NPr2 [42°] Formed from di propyl aniline (241°) and HNO₂ (Mandl, M 7, 99) Green trumetric crystals, a b c = 576 1 277 Yields quinone oximand dipropylamine on warming with potash

forms C H₃₇N,O [140°] NITROSO PROPYL CRESOL C₁₀H₁₃NO₂ ** C₆H_oMePr(NO)(OH) Cymoquinone oxim [140°] 18 formed from propyl cresol, KNO₂, and HOAc (Mazzara, G 12, 167) The isomeric

C.H. MePr(NO)(OH) melts at 167°

NITROSO RESORCIN C₆H₃(NO)(OH)₂[4 3 1] Oxy quinone oxim Formed from C6H4(OH)(ONa) and imyl nitrite (Fèvre, Bl [2] 39, 585, C R 96, 790) Golden crystals (containing aq), turning brown at 112° Its solution is turned deep green by a ferrous salt SnCl, reduces it to amido resorcin HO, yields nitroresorcin (Ulzer, M 9, 1128) —NH,A 2aq —KA'aq —NaA' —
AgA' brown needles

Methylether MeA' (Aronheim, B 12, 30) Ethylether EtA' Yellow flakes

Ethylether EtA'

D1 nitroso resorcin CoH (NO)2(OH)2[4 2 3 1] Formed by the action of nitrous acid on resorcin (Fitz, B 8, 631, Kostanecki, B 22, 1345) Yellowish plates (containing aq) Explodes at 115° Forms coloured lakes Yields di amidoresorcin on reduction -NH,A'-NaA' green powder

NITROSO RESORGIN DISULPHONIC ACID The salt C.H (NO)(OH)(OK)SO,K is formed by the action of KNO2 and HOAc on potassium re sorcin disulphonic acid (Ulzer, M 9, 1127)

forms violet crystals

NITROSO SUCCINIC ACID C,H,NO, ... CO.H CH. C(NOH) CO.H Obtained from its mono ethyl ether, which is got by allowing di nitroso succino succinic ether to stand with water (Ebert, A 229, 65) low 126° — CaA" 4aq Crystals, decomposing be-

Mono-ethyl ether EtHA" [111°] —
NH,EtA" — CaEt,A", 2aq — CaC,H,NO, 2aq —
BaC,H,NO, aq — Zn(EtA"), — AgEtA"
An isomeric ether EtHA" [54 7°] is obtained

by the action of NaOEt on the oxim of oxalacetic

ether (Piutti, O O 1888, 1460, 1890, 938, Hantzsch, B 23, 11)

Dr-ethylether Et2A". Oil Identical with the oxim of oxalacetic ether

Di nitroso succinic acid CO,H C(NOH) C(NOH) CO,H [130°] Formed from carboxy tartronic acid and hydroxylamine (Muller, B 16, 2985) Prisms —Ag₂A"

NITROSOSULPHATES NITROSO and SULPHURIC ACIDS v SULPHATES and SUL PHURIC ACID IN VOL 1V

NITROSO THIOGLYCOLLIC ACID

HS C(NOH) CO,H Formed by boiling nitrosothiohydantoin with baryta water (Maly a Andreasch, M 1, 168, B 13, 601) Crystals, v Gives a blue colour with FeCl, De sol ether somposed by boiling water or alcohol into CO, hydrogen sulphocyanide, and HO -BaA" aq

NITROSO - THIOHYDANTOÏN C,H,N,OS Formed from thiohydantoin and HNO2 (Maly, B 12, 967) Crystalline powder, al sol water

NITROSO - THYMOL v Oxim of THYMO-QUINONE

DI NITROSO - TOLUENE C,H,Me(NO), [6 3 2or1] [c 144°] Formed by oxidising tolu quinone dioxim with K3FeCy6 (Nietzki, B 21, 432, Mehne, B 21, 734) Amorphous insoluble powder, volatile with steam Gasified on fusion Reconverted by hydroxylamine into toluquinone dioxim

NITROSO o-TOLUIDINE C,H,NO C₆H₃Me(NO)(NH₂) [1 5 2] [116°] Formed by heating toluquinone mono oxim (nitroso o cresol, with acetate and chloride of ammonium (Mehne) B 21, 731) Small green needles with blue reflex Yields NH, and nitroso o cresol on heating with aqueous NaOH Hydroxylamine yields toluquinone dioxim

Nitroso-m-toluidine

 $C_0H_sMe(NO)(NH_2)$ [1 2 5] [178°] Formed in like manner from nitroso m cresol Resembles its isomeride and yields the same dioxim on treat ment with hydroxylamine

a-NITROSO-VALERIC ACID is the Oxim of

PROPYL GLYOXYLIC ACID

 γ -Nitroso-valeric acid CH₂ C(NOH) CH₂ CH₂ CO₂H Oxim of acetyl-propionic acid [96°] Formed from β acetylpropionic acid (levulic acid) and hydroxylamine (Muller, B 16, 1617) Prisms Yields levulic acid on treatment with tin and HCl H₂SO, at 100° forms methyl succinimide (Bredt, A 251, 816, cf Rischbieth, B 20, 2671) —BaA'₂2aq -AgA' white pp

Ethyl ether EtA' Oil

γδ-Di nitroso valeric acid CH(NOH) C(NOH) CH, CH, CO2H [1369] Formed from glyoxyl propionic acid and hy droxylamine (Wolff, A 260, 93) Prisms verted by conc H2SO, at 70° into furazyl propi

onic acid O N CH CH, CH, CO,H [86°]. -BaA'2 3aq thin needles

NITROSO-XYLENOL v Oxim of Xylo-OUINONE

180-NITRO STEARIC ACID C18H25(NO)O2

buttery mass, v sol ether and alcohol, insol. water and ligroin Yields stearic acid on reduction It is therefore not a true nitro compound. -K.A"-K.A"KHCO₃-Na₂A" granular mass, insol ether -SrA" -CuA', -CuA'' light g.een NITRO-STRYCHNINE v STRYCHNINE

NITRO-STYRENE The o, m, and p- 1somerides CoH4(NO) CH CH., melting at 14°, -5°, and 29° respectively, are formed by boiling the acids CoH,(NO) CHBr CH COH with aqueous Na CO₃ (Einhorn, B 16, 2213, Prausnitz, B 17, 597, Basler, B 16, 3005) The corresponding dibromides C, H, (NO)2 CHBr CHeBr melt at 520, 79°, and 73° respectively

ω-Nitro styrene C.H. CH CH NO2 (250° 260°) Formed by heating benzoic alde hyde with nitro methane and ZnCl, for 8 hours at 160° (Priebs, A 225, 319) Formed also by boiling styrene with HNO, (Simon, A 31, 269, Blyth a Hofmann, A 53, 297) Yellow crystals, yielding benzoic acid on oxidation freshly prepared it is soluble in NaOHAq, but the solution slowly decomposes, yielding benzoic aldehyde and resin Diluted H2SO, yields benzoic aldehyde, hydroxylamine, and CO Cone HClAq yields hydroxylamine and PhCHCl CO H [78°]

ωο-Di-nitro-styrene C_sH₄(NO) CH CH(NO₂) [107°] Formed, together with the wp isomeride, by nitration of ω nitro styrene (Priebs) Yellow

needles (from alcohol)

ωp Di-nitro styrene [199°] Formed as above, and also by the action of HNO, and H SO, on p nitro cinnamic acid at 0° (Fried lander a Mahly, A 229, 221, B 16,851) Yellow crystals, sol KOHAq Dilute H SO, decomposes it into p nitro benzoic aldehyde, hydroxylamine, and CO

ωm-Di-nitro-styrene [122°] Formed from m nitro cinnamic acid, HNO3, and H SO4 at 0' (Friedlander a Lazarus, A 229, 233) Yellowish plates (from water) Conc H₂SO₄ at 100° gives CO and m nitro benzaldoxim

o-NITRO STYRYL-ACROLEIN C11HoNO, 1 e C₆H₄(NO₂) CH CH CH CH CHO [153°] Formed from o nitro cinnamic aldehyde, aldehyde, and very dilute NaOH (Einhorn, B 17, 2026) Pale yellow crystals (from dilute alcohol)

o-NITRO-STYRYL ACRYLIC ACID

C_bH₄(NO₂) CH CH CH CH CO₂H [218°] Formed from o nitro cinnamic aldehyde, Ac,O, and sodium acetate, ind obtained also by oxidising C_eH₄(NO₂) C₄H₄ CO CH₅ with aqueous NaOCl (Diehl a Einhorn, B 18, 2331) Slender felted needles, v sol hot alcohol

o-NITRO STYRYL GLYOXYLIC ACID C₆H₄(NO₂) CH CH CO CO₂H [136°] Formed from o nitro benzoic aldehyde, pyruvic acid, and HClAq (Baeyer a Drewson, B 15, 2862) Crys Converted by alkalis into indigo

DI-m-NITRO-DI STYRYL KETONE [232°] Sparingly soluble flakes (Von Miller a. Rohde,

B 22, 1838)

o NITRO STYRYL METHYL KETONE C₆H₄(NO) CH CH CO CH₂ [60°] Formed, to gether with the p isomeride [110°], by nitration of styryl methyl ketone (Baeyer a Drewson, B Formed by boiling stearic acid (100 g) with 15, 2858, 16, 1953) Formed also by boiling HOAc (1500 c c) and HNO, (250 g of S G 148) C.H. (NO.) CH(OH) CH, CO CH, with Ac.O., or for four days (Claus, J pr [2] 43, 161) Yellowish C.H. (NO.) CH.CH CO CH, CO.CH, with dilute H₂SO₄ (Fischer & Kuzel, B 16, 35) Long | needles, sol alcohol

m NITRO STYRYL-QUINOLINE C17H12N2O2 C₆H₄C₄H₂N CH CH C₆H₄(NO₂) [132°] For ed by heating methyl quinoline (lepidine) with m nitro benzoic aldehyde and KHSO, at 160° (Heymann a Königs, \mathring{B} 21, 1429) Needles (from alcohol)

An isomeride [139°] is formed from (Py 3)methyl quinoline and m nitro benzoic aldehyde (Wallach, B 16, 2009, Wartanian, B 23, 3646) It gives the crystalline salts B'HCl -B'HNO.

B'C₆H₂(NO₂)₃OFA—B',H.PtCl₆ 1½aq
p Nitro styryl quinoline [165°] Formed 3) methyl quinoline and p nitrofrom (Py benzoic aldehyde (Bulach, B 20, 2047, 22, 285) Needles Yields a dibromide $C_{17}H_{12}N_1O_2Br_2$ [276°] which turns brown at 230°

NÎTRO DI-STYRYL DI-VINYL KETONE v NITRO PHINYL BUTINYL PHENYL BUTINYL KETONE

NITRO o SULPHO-BENZOIC ACID C_7H_5NSO $i \in C_6H_3(NO_2)(SO_3H)(CO H)$ [4 2 1] [110] Formed by oxidising intro toluene sulphonic acid (Hart, Am 1,350, Hedrick, Am 9,411, Kastle, Am 11, 177) White needles (from hot water) -KHA"aq long needles -K,A" -BaA" Chloride C,H,(NO₂)(SO₂Cl)(COCl) [60]

Amide C,H,(NO2)(SO2NH2)(CO2H) [172°] Formed by oxidising p nitro toluene sulphonic amide with K3FeCy or alkaline KMnO4 (Noyes, Am 8, 171, 11, 161) Small granules (from hot water), melting at 177° when slowly heated, but at 172' when quickly heated Changes slowly when kept at 180° into the anhydride $C_{_0}H_{_3}(NO_{_2}) < SO_{_2} > NH[209^{\circ}]$ which yields the salts KC, H, N, SO, S 96 at 18 5°, Ba(C H, N SO), 3aq, and AgC H, N2SO, The free amic acid yields the salts Ba(CH N2SO₆)2 aq, AgC, H3N2SO₆ laq, and Ag2C7H, N, SO, aq

Nitro m sulphobenzoic acid $C_iH_i(NO)(SO_iH)(COH)[r + 1]$ Formed by m trating m sulphobenzoic acid (Impricht a Uslar, A 106, 27) Crystalline — BaA" 3aq — BaA" 1'aq BaH₂A"₂ 4aq 1 idiating prisms

Nitro p sulphobenzoic acid

 $C_1H_1(NO)(SO_3H)(CO_2H)$ [2 4 1] Formed by oxidising (2, 1, 4) intro toluene sulphonic acid (Hart Am 1, 352) - KHA" - BaA" 2aq granules

Nitro p sulphobenzoic acid $C_8H_8(NO_3)(SO_3H)(CO_2H)$ [3 4 1] [181°] Formed by nitrating p sulphobenzoic acid (Hart, Am 1, 342, Remsen, A 178, 288) Prisms — KHA" 1 aq — BaA" 4aq — BaH₂A", 6aq — CaA" 5aq — CuA" 5aq bluish green crystals

NITRO BULPHO TOLUÏC ACID C.H.NSO, te $C_0H_2Me(NO_2)(SO_3H)(CO_2H)$ [1 6 4 3] Formed by oxidation of nitro m xylene sulphonic acid C_eH₂Me₂(NO₂)(SO₃H) [1 3 6 4) with KMnO₄ (Limpricht, B 18, 2191) -A'K taq fine white

silky needles

NITRO SULPHYDRO CINNAMIC ACID C_eH₄(NO₂) CH C(SH) CO H [240°] Formed from C_eH₅ CH C(SH) CO SCN, natric acid and H₂SO, (Bondzynski, M 8, 355) Crystals (from alcohol)—BaA'₂ long needles
NITRO α-SULPHYDRO CINNAMOYL SUL Crystals (from

PHOCYANIDE C.H.(NO.) CH C(SH) CO SCN The o- compound [189°] is formed, together with the p- derivative [251°] by nitrating sulphydro cinnamoyl sulphocyanide These bodies may also be got from thioglycollyl sulphocyanide and the corresponding nitro - benzoic aldehyde

(Bondzynski, M 8, 355) Both are crystalline NITRO-SULPHYDRO METHYL IMIDAZOLE HNO, (Wohl a Marckwald, B 22, 1358) Yellow needles, sl sol cold water -B',H PtCl [197°

NITRO SULPHYDRO PHENYL IMIDAZOLE Methylderivative C,HN,Ph(NO,)(SMe) Formed from NPh C(SMe) N and [116°] dilute HNO, (Wohl a Marchwald, B 22, 1357)

NITROSYL BROMIDE, CHLORIDE, and SUL **PHATE** v Nitrogen oxybromides and oxychlorides,

p 569, and Nitro sulphonic acid, vol iv p 601 NITRO TEREPHTHALIC ACID C.H.NO. 1 e $C_6H_3(NO_2)(CO\ H)_2[2\ 4\ 1]$ [270°] Formed by nitriting terephthalic acid (De la Rue a Muller, A 121, 90, Burkhardt, B 10, 145) Crystalline A. A" powder (Skraup, M 7, 148)

Methyl ether Me, A" [70°]

Prisms (Ahrens, B 19, 1636)

Amide C₆H₃(NO₂)(CONH)₂ Prisms NITRO TEREPHTHALIC ALDEHYDE

C,H,(NO2)(CHO), [86°] Formed from terephth the aldehyde, KNO, and H2SO, at 110° (Löw, A 231, 364) Large needles (by sublimation) With acctone and NaOH at 60° it gives the indigo reaction

NITRO THIENOL C4H2S(NO2)(OH) [116°] Formed by treating a dilute H₂SO, solution of amido thiophene with nitrous acid and boiling for some time Colourless needles Sol water and ether Dissolves in alkalis with a yellow colour (Stadler, B 18, 2319)

NITRO-(a)-THIENYL-GLYOXYLIC ACID C,H2(NO)S'CO CO.H [92°] Formed by oxida tion of nitro thienyl methyl ketone [123°] (Peter, B 18. 541) Crystals

NITRO (a) THIENYL METHYL KETONE C,H,(NO2)S'CO CH3 Two 150merides [86°] and [123°] are formed by nitiating (a) thienyl methyl ketone with fuming HNO, at -8° (Peter, B 17, 2646, 18, 541) They both yield the same di nitro thienyl methyl ketone [167°]

m NITRO THIOBENZOIC ALDEHYDE $(C_0H_4(NO_2) CHS)_x$? A grey powder formed by passing H2S into an alcoholic solution of m nitro benyoic aldehyde (Bertagnini, A 79, 269) Insol.

ordinary solvents NITRO THIONYL ANILINE

C.H.(NO) N(SO) Formed from nitro-aniline and thionyl chloride (Michaelis a Humme, B 24 755) The *m* compound melts at 63 5°, the *p* isomeride at 70° Decomposed by hot water

NITRO THIOPHENE C.H. (NO.)S (225° co1) Prepared by passing air charged with thiophene vapour through fuming HNO. (Meyer a Stadler, B 17, 2648, 18, 533) yellow monoclinic prisms

Di nitro thiophene C,H,(NO,),S (290°) Formed, together with the isomeride [78°], by further intration of intro thiophene (Meyer a Stadler, B 17, 2648, 2779, 18, 530, 1778) Yellow monoclinic plates, m sol water Converted by repeated steam distillation into the isomeride [78°] A drop of KOHAq added to the alcoholic solution gives a splendid red colour, destroyed by excess of KOH. Forms the double compounds C₄H₂(NO₂)₂SC₁₀H₃ [50°] and | C, H2(NO2), SC14H10 [162°]

Di-nitro-thiophene [78°] Formed as above

Yellow needles, volatile with steam

NITRO THIOPHENE SULPHONIC $C_4H_2(NO_2)(SO_3H)S$ Formed from nitro thiophene and fuming H.SO. (Stadler, B 18, 534)
White hygrosopic crystals —AgA'

Oıl Chloride

Amide C,H,(NO,)S(SO,NH,) [178°] NITRO (a) THIOPHENIC ACID C,H,NSO, i e C₄H₂S(NO₂)(CO₂H) [146°] Formed from (a) throphenic acid and cone HNO₂ at 50° (Romer, B 20, 116) Needles, slowly changed by water into a variety melting at about 125° A little NaOH colours its alcoholic solution magenta

CuA'_2—AgA' needles

Ethylether EtA' [71°]

NITRO THYMOL C₆H₂Me(C₅H₇)(NO₂)(OH) [140°] Formed by oxidation of nitroso thymol (R. Schiff, B 8, 1501, Liebermann, B 10, 612) Di nitro-thymol [55°] Formed by nitration of thymol or its sulphonic acid (Lallemand, A Ch [3] 49, 152) Crystalline — KA' — BaA', 3aq —CaA', 5aq —AgA' lemon yellow pp

Ethyl ether Eth [53°] Tables (from alcohol) (Ladenburg a Engelbrecht, B 10, 1218) Tri-nitra-thymol [111°] Got by nitrating di nitro thymol Yields a methyl ether [92°]

(Atcherley, Z 1871, 415)

NITRO-TOLUAMIDOXIM CaHaNaO $\mathbf{C}_{6}\mathbf{H}_{2}\mathbf{M}_{9}(\mathbf{NO}_{2})$ $\mathbf{C}(\mathbf{NOH})(\mathbf{NH}_{2})$ [4 2 1] [161°] Formed by heating nitro toluic nitrile with alco holic hydroxylamine (Weise, B 22, 2430) Needles -B'HCl white crystalline mass

o NITRO-TOLUENE O-TOLUENE C.H.Me(NO.) [1 2]
(218°) S.G. 15 1 168 (Streng, B. S.V. 142 3 (Lossen, A. 254, 73) Mol w 137 24, 1987) Formed, together with the p isomeride, by ni tration of toluene (Glénard a Boudault, C R 19, 505, Hofmann a Muspratt, A 53, 221, Kekulé, Z [2] 3, 225, Rosenstiehl, A Ch [4] 27, 433) Formed also by elimination of NH, from (2, 1, 4) nitro p tolundine (Beilstein a Kuhlberg, A 155, 1, 158, 348) Inquid, solidifies at After administration to dogs it appears in the urine as o-nitro benzoic acid and crys talline C14 H19 N3O10 2 2 aq (Jaffé, Russ Zent Pharm 1878, 513, Noyes, Am 5, 99) Long boiling with alkaline K_3 FeCy_e yields o-nitro benzoicacid Zinc dust and alcoholic NaOH reduce it to oazoxy toluene [59°] (Guitermann, B 20, 2016) Its product of sulphonation differs from that of p-nitro toluene in giving no red colour when boiled with alkalis (Reverdin a Harpe, Bl [2] 50,

m Nitro-toluene C₆H₄Me(NO₂) [1 3] [16°] (230°) SG ²² 1 168 SV 144 0 Occurs in small quantity in crude nitro toluene (Monnet, Reverdin, a Nolting, B 12, 445, 18, 1837) Prepared from o- or p-toluidine by successive acetylation, nitration, saponification, diazotisation, and boiling with alcohol (Beilstein a Kuhlberg, A 155, 24, 158, 346, Buchka, B 22, 829) Yields m-nitro-benzoic acid on oxidation SnOl, in HClAq reduces it to pure m toluidine, while zincdust and HClAq yield chloro m-toluidine also Boiling with KOH in MeOH forms (C.H.Me), N.O

[89°] p-Nitro-toluene O.H.Me(NO.) [1.4]

(234°) (Streng). S.V S.121.7 (Schiff, A 223, 261).

Formed, together with the o-isomeride, by nitration of toluene Trimetric crystals Much less volatile with steam than o-nitro-toluene Oxidised by boiling alkaline K.FeCy, to p nitro-benzoic acid (Noyes, B 16, 52) Reduced by iron and HClAq to pure p-toluidine, while zinc and and NoIAq we pure p-volutine, while zinc and HClAq yield chlorinated toluidine. Zinc dust and NaOH reduce it to (C₆H,Me)₂N₂ [144°], two azoxy compounds (C₆H,Me)₂N₂O [75°] and [70°] and (C₆H,Me)₂N₂H₂ [126°] (Janovsky a Reimann, B 22, 40) Cro₂Cl₂ followed by water yields nitro toluquinone (Étard, C R 87, 989) NaOMe yields a brownish red product neduced by SnCl₂ to C₂H₂(C₂H₄NH₂)₂ (Bender a Schultz, B 19,

ω-Nitro-toluene C₆H₅ CH₂(NO₂) Phenylnetro-methane Formed by the action of acids upon the di sodio-derivative of nitro benzylidene

 $C(ONs) = C(Ns)NO_{2}C_{6}H_{6}$ phthalide CaH

briel a Koppe, B 18, 1254, 19, 1145) Liquid, boiling with decomposition at 226° Reduced by tin and HCl to benzylamine By heating with fuming HCl at 150° it yields benzoic acid and hydroxylamine Gives a white crystalline sodium derivative

D1-nitro-toluene C₂H₂Me(NO₂), [1 2 4] Mol w 182 [70°] (300°) SVS 137 5 (Schiff) S (CS₂) 2 19 at 17° Obtained by nitration of toluene (Deville, A 44, 307, Cahours, C R 24, 555, Nölting a Witt, B 18, 1336) and o or p nitro toluene Obtained also by eliminating NH, from di-nitro toluidine [195°] (Staedel, A 259, 220) Monoclinic needles, al. sol cold alcohol Yields tolylene m diamine on reduction (Baeyer, B 7, 1638) By partial reduction with ammonium sulphide the p-nitro-group is reduced, giving $C_8H_3Me(NO_2)(NH_2)$ [1 2 4] of melting point [78] On the other hand, by alcoholic SnCl₂ (3 mols) C₂H₃Me(NH₂)(NO₂)[1 2 4] of melting point [107°] (Anschutz a Heusler, B 19, 2161)
s-Di-nitro-toluene C₂H₃Me(NO₂)₂ [1 3 5]
[93°] Formed by eliminating NH₂ from di

[166°] (Staedel, B 14, 901, A 217, 189, Nevile a Winther, C J 41, 416, Hubner, A 222, 75) Yellow needles (from HOAc mixed with benz ene), v sol benzene and alcohol Volatile with steam Yields di nitro benzoic acid [204°] on oxidation

Di-nitro-toluene C₆H₃Me(NO₂)₂ [1 2 3] [63] Formed by heating (2, 3, 1, 4) di nitro toluic acid with dilute HClAq (Rozanski, B 22, 2681) Hair-like needles (from dilute HOAc)

Di-nitro-toluene $C_8H_3Me(NO_2)_2$ [1 2 5] [48°] **a** L), [52 5°] (R) Formed by heating (1, 4, 8, 6) di nitro toluic acid with dilute HClAq at 250° (Rozanski, B 22, 2679) Formed also from toluquinone dioxim and HNO, (Nietzki a Guitermann, B 21, 428) Yellow crystals (from lıgroïn) Appears also to occur among the products of the nitration of toluene (Limpricht, B 18, 1402)

Di-nitro-toluene O₆H₃Me(NO₂)₂ [1 2 6] [61°] Formed by eliminating NH₂ from di nitro p toluidine [168°] (Staedel, A 217, 206, 225, 884) Formed also by nitration of toluene Needles

(from alcohol).

Di-nitro toluene C₆H₄Me(NO₂)₂ [1 3 4]? [60°] **S** (CS₂) 2 188 at 17° A product of nitration of m-nitro toluene (Beilstein a Kuhlberg) Long

needles (from CS2)

(a) Tri-nitro-toluene C₀H₂Me(NO₂), [1 2 4 6] Mol w 227 [82°] S (CS₂) 386 at 17° Formed by nitration of toluene (Wilbrand, A 128, 178) Flat needles, v sol hot alcohol Forms with aniline a compound C₆H₂Me(NO₂)₂PhNH₂ [84°] (Hepp, A 215, 365)

(β) Tri nitro toluene C_eH₂Me(NO₂)₃ [112°] Formed, together with the (γ) isomeride, by ni tration of m nitro toluene (Hepp) Triclinio

prisms (from acetone)

(γ) Tri nitro toluene C_sH₂Me(NO₂), [104°] Formed as above (Hepp) Trimetric place b c = 937 1 672 V sl sol cold alcohol Trimetric plates,

NITRO TOLUENE w PHOSPHONIC ACID

C₆H₄(NO₂) CH₂ PO(OH)₂ Formed by dissolving toluene w phosphonic acid in fuming HNO. (Litthauer, B 22, 2144) Yellow needles, de composing at 217° without melting The acid (C_sH₄(NO₂) CH),PO OH melts at 212°

NITRO TOLUENE SULPHINIC ACID

C₆H₃Me(NO₂) SO H Formed by reduction of C.H.Me(NO2) SO2Cl by sodium amalgam (Otto a Gruber, A 145, 24) Crystalline —NaA' aq

Di nitro toluene sulphinic acid C₆H₂(CH₃)(NO₂), SO₂H Formed by reduction of di nitro toluene sulphonic chloride with zinc dust (Perl, B 18, 71) V sol water and alcohol Salts -A'K.-A'2Ba -A'2Pb 3aq

prisms o NITRO-TOLUENE SULPHONIC ACID

 C_sH , $Me(NO_s)(SO_3H)$ [1 2 5] Formed from C.H Me(NO)(NH)(SO,H) [1245] by heating its diazo derivative with alcohol at 100 (Foth, A 230, 305)

Chloride C, H, Me(NO,)(SO,Cl) [50°]. Amide [1335°] Long needles

o Nitro toluene sulphonic acid

C, H, Mc(NO₂)(SO₃H)[1 2 4] Formed by sulpho nating o nitro toluene or by nitrating toluene p sulphonic acid (Beilstein a Kuhlberg, A 155, 18, Engelhardt a Bek, Z [2] 5, 209, Kornatzki, A 221, 180)

Salts —BaA', 2aq S (of BaA',) 58 at 19 5° —PbA', 2aq S (of PbA',) 77 at 18° Chloride Oil (Otto a Gruber, A 145, 23)

Amide [128°] (O a G), [139°] (K), [144°] reale, A 203, 73) Yields a benzoyl derivative (Neale, A 203, 73) C₆H₁Me(NO₂) SO₂NHB₂ [130°] whence the salts C.H.Me(NO) SONKBz, $Ca(C_{14}H_{11}N_2SO_5)_2$ 2aq and Ba(C₁₄H₁₁N₂SO₅), may be prepared, and whence PCl, produces C₄H₃Me(NO₂) SO₂N CClPh [125°] from which ammonium carbonate forms C, H, N, SO, [128°] (Anna Wolkoff, Z 1871, 422, B 5, 141)

p Tolunds [181°] Orystals o-Nitro-toluene sulphonic acid

C.H.Me(NO2)(SO.H)[1 2 8, 5 or 6] Formed from (2, 1, 4) nitro toluidine by sulphonating and eliminating NH, (Foth) Its salts are v e sol water

Chlorade [50°] Thick Thick prisms o-Nitro toluene sulphonic acid

C.H.Me(NO.)(SO.H)[1 2 or 6 8] Formed from ptoluidine sulphonic acid by nitration and elimimation of NH, (Pechmann, 4 178, 214, Foth,

A 280, 308) -BaA', 2aq plates, sl sol cold water

Chloride C.H.Me(NO,)SO,Cl Amide $C_6H_3Me(NO_2)SO_2NH_2$ [163 5°]

m Nitro-toluene sulphonic and Formed by sulphonating m nitro toluene (B a K) — BaA', 2aq S (of BaA',) 1 145 at 175°— PbA' 2 2 aq S (of PbA' 2) 3 62 at 18°

p-Nitro toluene sulphonic acid

 $C_{s}H_{3}Me(NO_{2})(SO_{2}H)[142]$ [134°] S 210 at 23°, 250 at 28° Formed by sulphonating p nitro toluene (Javorsky, Z 1865, 222, B a K, Jenssen, A 172, 230, Hart a Remsen, B 10, 1046, Am 1, 349, Schwanert, A 186, 351, Noyes, Am 8, 168, Hausser, Bl [3] 3, 797) Trimetric crystals (containing 2 aq) NaOHAq yields an azoxy compound reduced by zinc dust to di amido stilbene disulphonic acid

Salts-NH,A' long prisms, not lecomposed by H₂SO₄ at 100° -NaA' 2aq -KA' 262 at 16°—BaA', 3aq S 334 at 185—CaA', 4aq—CaA', aq—CaA', 26q —PbA', 3aq S. (of PbA',) 15 3 at 19°—PbA', 2aq

Chloride [44°] Tablets (from ether) Amide [187°] Needles

Nitro-toluene exo-sulphonic acid $[1 4]C_6H_4(NO_2)$ CH₂ SO₃H Formed by nitra

tion of O.H. CH.SO.H (Mohr, A 221, 217)

Chloride Oil When gently distilled it gives SO. and C.H. (NO.) CH.Cl[14] [715°]

Amide [204°] Prisms Accompanied by an isomeride $[140^{\circ}-160^{\circ}]$

Nitro-toluene disulphonic acid

C.H.Me(NO.)(SO.H), Formed by boiling p brome toluene disulphonic acid with fuming HNO. (Kornatzki, A 221, 198)—K.A" The same, or an isomeric acid, is obtained by dis placing Br by H and nitrating the product, it gives the salts K.A" and BaA" 3aq

Di-nitro-toluene exo-sulphonic acid C₆H₃(NO₂), CH SO₃H Formed from the acid C₆H₄(NO₂) CH, SO₃H and a mixture of H₂SO₄ (2 pts) and fuming HNO, (1 pt) (Mohr, A 221,

225) - KA' - BaA', 4aq - PbA', 4aq

Di-nitro-toluene sulphonic acid [165°] C.H.Me(NO.),SO.H[1 2 6 4] by nitrating toluene p sulphonic acid (Schwanert, B 10, 28, A 186, 342) Trimetric prisms (containing 2aq)—KA'S 52 at 145°S (94 pc taining 2aq) —KA' S 52 at 145° S (94 p c alcohol) 09 at 22°—NH, A' S 42 at 18°— BaA', 4aq S 8 at 17° -CaA' 2aq -PbA', 2aq PbA' 3aq S (of PbA',) 2 64 at 14 5° (B a K., Z [2] 6, 796)

Chloride [125°] Crystals (from ether) [203°] Laminæ Amide

(a) NITRO-o-TOLUIC ACID C.H.NO. $C_{2}H_{3}Me(NO_{2})(CO_{2}H)[2\ 5\ 1]$ [179°] Formed. together with the (β) acid, by nitration of o toluic acid, and, together with the (γ) acid by oxidation of nitro-o-xylene with dilute HNO, (Jacob sen, B 16, 1957, 17, 162) Small crystals, v. sl sol water Yields amido toluic acid [196°] and oxy toluic acid [172°] — KA' aq — CaA', 2aq —BaA', 2aq slender needles (β) Nitro-o-toluic acid

C₆H₂Me(NO₂) CO₂H [2 8 1] [145°] Formed as above. Long needles Yields oxy toluic acid above. Long needles Yield [188°] —BaA', 2aq —CaA', 2aq

)-Nitro-o-toluic acid

C.H.Me(NO.) CO.H [2.4 1]. [152°]. Formed as

above Long needles Yields oxy toluic acid [179°] —BaA', 5aq easily soluble prisms

(a)-Nitro-m-toluic acid C,H,Me(NO2) CO2H [3 6 1] [219°] Formed, together with a small quantity of its (3, 2, 1) isomeride [182°], by nitration of *m* toluic acid (Jacobsen, *B* 14, 2353, Ahrens, *Z* 1869, 183, Krausler, *Z* 1866, 370, Panaotovic, *J pr* [2] 33, 64) Monoclinic prisms—BaA', 2aq— 83, 64) Monoclinic CaA's 4aq m sol water

(β)-Nitro m-toluic acid C₆H₃Me(NO₂)CO₂H

[3 2 1] [182°] Formed as above (Jacobsen) s Nitro-m-toluic acid

C₆H₃Me(NO₂)CO₂H[3 5 1] [167°] Formed by oxidation of s-nitro m-xylene with KMnO₄ and acetic acid (Thöl, B 18, 360) Silky needles, v sol water -BaA' 4aq S 308 at 15° Needles

Nitro m toluic acid $C_0H_3Me(NO_2)CO_2H[8 4 1]$ [214°] Formed by oxidation of crude nitro-xylene (Beilstein a Kreusler, A 144, 168, Remsen a Kuhara, Am 3, 426) and of nitro isocymene (Kelbe, A 221, 161) - NH, A' 2aq - MgA', 7aq - CaA', 2aq -

BaA', 4aq very soluble needles
Ethyl ether EtA' [55°]
Amide [151°] (B a K]
Nitrile C.H., Me(NO.) ON [55°] (B a. K)

Nitro-p-toluic acid $C_{\mathbf{g}}\mathbf{H}_{\mathbf{g}}\mathbf{M}\mathbf{e}(\vec{NO}_{\mathbf{g}})(\mathbf{CO}_{\mathbf{g}}\mathbf{H})$ [4 3 1] [190°] Formed by boiling cymene or p-toluic acid with fuming HNO, (Noad, A 63, 297, Fittica, A 172, 309, Fittig, A 168, 251, Ahrens, Z [2] 5, 102) Monoclinic prisms, sl sol cold water -BaA'₂4aq —CaA'₂3aq —CuA'₂4aq —Cu₃A'₄(OH) —Cu₂A'₄(OH) aq (Noyes, Am 10, 472) — Pb(OH)A' —AgA' The ethers MeA' and EtA' are crystalline

Nitro-p-toluic acid $C_0H_2Me(\bar{NO}_2)(CO_2H)$ [4 2 1] [161°] Obtained by heating its nitrile with HClAq at 195° Long needles -BaA', 4aq -BaA', 5aq (Noyes, Am 10, 472) —CaA', 2aq —CuA', aq —AgA' needles

Amide [153°] Slender needles

Netrele C.H.Me(NO2)CN [99°] (G, W), [101°] (N) Formed from (3, 1, 4) nitro-p-toluid-ine by Sandmeyer's reaction (Glock, B 21, 2662, Weise, B 22, 2429, Von Niementowski, J pr [2] 40, 4, 21, 1535, 1992) Needles (from alco Yields on reduction with tin and HCl the compounds (C_eH_sMeCy)₂N₂O [182°] and C_eH_sMe(NH₂)CN [94°] Does not form an imidoether when treated with alcoholic HCl (Pinner, B 23, 2919)

A nitro toluic acid [218°] was obtained by Ahrens together with the acids [219°] and [190°] by the action of HNO, on crude xylene

Di-nitro-o toluic acid

 $C_aH_2Me(NO_2)_2CO_2H[2 5 3 1]$ Formed [206°] by nitrating o toluic acid (Jacobsen a Wierss, B 16, 1957, Racine, A 239, 77) Needles Yields di nitro-phthalic acid [226°] on oxidation— BaA', 2aq v e sol water Methylether MeA'

[74°] Needles Di-nitro-p toluic acid

 $O_2H_2Me(NO_2)_2CO_2H$ [4 3 5 1] $[158^{\circ}]$ Formed by nitrating p toluic acid (Brückner, B 8, 1678) Plates (from hot water) — KA' 2aq — CaA', 2aq —

BaA'₂2aq —AgA' Di-nitro p toluic acid O₂H₂Me(NO₂) CO₂H [4 2 5 1] [1889] Formed, together with the isomeride [249°], by nitrating

(2, 4, 1)-nitro toluic acid (Rozansky, B 2676) Radiating needles Yields (1, 4, 8) dinitro toluene on heating with dilute HCl at

Di nitro-p-toluic acid

C₀H₁Me(NO₂)₂CO₂H₁(4 2 3 1] [249°] Forme
as above (R) Trimetric prisms —CaA'₂ aq

A', 4aq long needles NITRO m-TOLUIC ALDEHYDE C, H, NO, 16 C,H,Me(NO2)CHO An oil, formed as well as di nitro m toluic aldehyde [112°], by nitrating m toluic aldehyde (Bornemann, B 17, 1473)

NITRO-0-TŎLUÌDINE $C_6H_3Me(NH_2)(NO_2)[1\ 2\ 8]$ [9**7**°] Obtained from acetyl o-toluidine by nitration and saponi fication (Lellmann a Wurthner, A 228, 240), and also by heating its sulphonic acid with dilute H₂SO, at 180° (Nietzki a Pollini, B 23, 138) Prisms (from dilute alcohol)

[158°] Acetyl derivative Plates Nitro-o-toluidine CeH3Me(NH2)(NO2) [1 2 4] [107°] Obtained by nitrating o toluidine (1 pt) dissolved in H₂SO₄ (10 pts) (Nölting a Collin, B 17, 268) and by reduction of (4, 2, 1) di nitro toluene [70 5°] (Graeff, A 229, 343, Limpricht, B 18, 1400, Anschutz, B 19, 2161) Orange monoclinic prisms Sweet taste -B'-H-SO.

plates, decomposed by water Acetyl derivative [151°] Needles Nitro-o toluidine CoH, Me(NH2)(NO2) [1 2 5] [128°] Obtained from its acetyl derivative which is got by nitrating acetyl o toluidine (Beil stein a Kuhlberg, A 158, 345) Small lemon

yellow needles (from water)

Acetyl derivative [197°] Needles Nitro o toluidine C.H.Me(NH.)(NO.) [1 2 6] Formed by reduction of (6, 2, 1) di nitro toluene (Cunerth, A 172, 223, Ullmann, B 17, Formed also, together with the (1, 2, 4) isomeride, by nitrating o toluidine in presence of a large excess of H₂SO, (Green a Lawson, priv com) Bright yellow slender needles —B'HCl

Acetyl derivative [158°] Needles Benzoyl derivative [167°]

Nitro m toluidine C₆H₃Me(NH₂)(NO₂)[1 3 6] [184°] Formed from its acetyl derivative, which is got by nitrating acetyl m toluidine (Beilstein a Kuhlberg, A 158, 348) Obtained also by heating the ethyl ether [54°] of nitro cresol [129°] with NH,Aq at 150° (Staedel, A 250, 214) Needles, v sol alcohol Yields tolylene p diamine [64°] on reduction (Fileti a Crosa, G 18, 298)

Acetyl derivative [102°] Nitro m-toluidine C6H3Me(NH2)(NO2)[1 3 4] [109°] Formed by heating the ethyl ether [51°] of nitro-cresol [56°] with NH₃Aq for 8 hours at 150° (Staedel, A 259, 225) Golden plates, m sol alcohol

s Nitro m toluidine

C₂H₂Me(NH₂)(NO₂)(1 3 5] [98°] Formed from s di nitro toluene (Becker, B 15, 1138, Nevile a Winther, C J 41, 416, Staedel, A 217, 199) Needles—B'HCl [56°] Prisms

Bensoyl derivative [1779

Natro m toluidine C.H. Me(NH.)(NO.) [1 3 2] [58°] Formed by reducing (2, 3, 1) di nitrotoluene (Limpricht, B 18, 1401)—B'HCl.— B'aH2SO, tables, v sol hot water

Acetyl derivative [186°] Needles Witro-p-toluidine CaHaMe(NH2)(NO2)[1 4 3]. [116°] Formed from acetyl-p toluidine by nitra tion and hydrolysis (Belistein a Kuhlberg, A 155, 23, Lorenz, A 172, 177, Hubner, A 208, 813, Cosack, B 13, 1088, Ehrlich, B 15, 2009, Gattermann, B 18, 1483, Lellmann, A 221, 7, Nölting, B 17,263) Formed also by heating nitrop cresol with NH, Aq at 180° (Barr, B 21, 1543) Red monoclinic prisms, $a \ b \ c = 135811755$, $\beta = 54^{\circ} 51'$ (Panebianco, $G \ 9,358$)—B'HCl— B'HNO₃ crystals, decomposed by water

Acetyl derivative [95°] Needles duced by means of ammonium sulphide at 0° to ${C_6H_3Me(NHAq)}_2N_2O$ [196°] and the compound $C_6H_3Me < NH CMe > 0$ [234°], whence B'HCl, B'.H. PtCla, and B'HNO, (Bankievitch, B 22,

Trichloroacetyl derivative [55°]. Valeryl derivative [88°] Yields on reduction $C_6H_4Me < NH > C C_4H_6$ [145°]

Benzoyl derivative [143°] Needles

Nitro p toluidine C_eH₂Me(NH₂)(NO₂) [1 4 2] [77 5] [77 5 Formed by reduction of (4, 2, 1) dinitro toluene (B a K) and, together with a small quantity of the preceding isomeride, by the action of nitric acid on a solution of p toluidine m H₂SO₄ (Hubner, B 10, 1716, Nolting a Collin, B 17, 203, Γoth, A 230, 299) Mono-Monoclinic needles —B'HCl [220] —B'HNO₃ — B',H SO₄ 2aq stellate needles — B',AgNO₃ 1132~1 Greenish yellow crystals (Mixter, Am 1, 241)

1 cety l derivative [144 5°] (Wallach, A 234, 353) Needles

Benzoyl dernative [172°] Pale yellow prisms (Bell, C N 30, 202)

Di-nitro-o toluidine

 $C_6H \text{ M}_{\epsilon}(\text{NH}_2)(\text{NO}_2)_2 [1\ 2\ 3\ 5]$ [208°] Formed from di nitro o cresol and its ethers by the action of NH, (Staedel, B 14, 900, A 217, 185, 203, Van Romburgh, R T C 3, 398, Barr, B 21, 1543) Yellow pusms (from xylene)

Di-nitro-m toluidine

C_bH Me(NH)(NO) [1346] [193°] Formed from the ethyl other of dinitro m cresol and NH, Aq at 100° (Staedel, A 259, 220), and from C_6H MeBr(NO₂)₂ and NH₃ (Jackson, B 22, 1232) Formed also by reducing (γ) tri nitro toluene (Hepp, A 215, 368) Yellow crystals, yielding di nitro toluene [71°] on elimination of NH.

Di - nitro - p - toluidine C_sH₂Me(NH₂)(NO₂) [1 4 3 5] [168°] S (CS2) 32 at 18° Formed by nitration of acetyl or benzoyl p toluidine and hydrolysis of the product (Beilstein, B 13, 242, Hubner, A 222, 73) Formed also by the action of ammonia on the ethers of di nitro p cresol (Staedel, A 217, 183) Needles, sl sol alcohol Yields chrysanisic acid on oxidation

A cetyl derivative [195°] Needles Yields on reduction an azoxy-compound [236°], an azo-compound [244°], and C₀H₂N₂O₃ [256°] The compounds $C_6H_2Me(NO_2) < \frac{N}{NH} > CMe [246^\circ]$ and

 $C_eH_aMe(NH_2)$ $\stackrel{NH}{\sim}$ $\stackrel{CMe}{N}$ $\stackrel{O}{\sim}$ O [266°] may also be

got by reduction (Bankievitch, B 21, 2404) Trichloroacetyl derivative [1420]. Prisms or needles (Friederici, B 11, 1975)

Bensoyl derivative [186°] Needles Vol III

An isomeric body [203°] is got by nitrating benzoyl-(2,1,4) nitro toluidine (Cunerth, A 172, 229).

Di - nitro - p - toluidine C_eH₂Me(NH₂)(NO₂)₂ [1 4 2 6] [168°] Formed from tri nitro-toluene [82°] and ammonium sulphide (Tiemann, B 3, 218, Beilstein, B 13, 242, Staedel, A 225, 384). Needles, v sol alcohol

Di nitro - p - toluidine $C_eH_2Me(NH_2)(NO_2)_2$ [94°] Formed by heating (β) tri nitro toluene with alcoholic NH_2 at 100° (Hepp) Golden needles (from HOAc)

Tri-nitro-m-toluidine C_eHMe(NH₂)(NO₂)₈ B 2 4 6 [136°] Formed by the action of [1 3 2 4 6] [136°] NH, on the ethyl ether of transtrom cresol (Nolting a Salis, B 15, 1864, A Ch [6] 4, 128, Staedel, A 259, 222) Small cubes, sol alkalis, forming a red solution

NITRO-p-TOLUIDINE SULPHONIC ACID $C_6H_2Me(N\hat{H}_2)(NO_2)(SO_3H)[1\ 4\ 2\ 5]$ S 1603 at 15° Formed by sulphonating nitro-p toluidine (Limpricht, B 18, 2183, Foth, A 230, 298) -KA'aq —BaA'₂4aq —PbA'₂3½aq?

DI-NITRO TOLYL-ACETIC ACID

 $C_{\rm e}H$ Me(NO₂) $CH_{\rm 2}$ $CO_{\rm 2}H$ [173°] Formed by nitration (Senkowsky, M 9, 856) Yields the ethers MeA' [41°] and EtA' [68°] crystallising in needles

NITRO p-TOLYL-AMIDO-ACETIC ACID $[1 \ 3 \ 4] C_6 H_3 Me(NO_2) NH CH. CO_2 H$ Formed from nitro p toluidine and bromo acetic acid (Plochl, B 19, 9, Leuckhait B 20, 24) Prisms — NH_4A' — $BaA'_{2}\frac{1}{2}aq$ — PbA'_{2} purple red needles

Ethyl ether EtA' [65°] Needles

NITRO O TOLYLAMIDO BENZOIC ACID [3 4 1] C₆H₃(NO₂)(NHC,H) CO₂H [211°] Formed by heating o toluidine with bromo nitrobenzoic acid (Heidensleben, B 23, 3451) Brown

needles - NaA' xaq red needles Ethyl ether EtA' [106°] [106°] Leaflets m Nitro p tolyl amido benzoic acid

C₆H₄Me NH C₆H₃(NO₂) CO H [257°] Formed from p tolundine and bromo nitro benzoic acid (Schöpff, B 22, 3288, H) -NaA' dark red needles

Ethyl ether EtA' [115°] Leaflets

NITRO DI p TOLYL AMINE
NH(C H)(C,H,NO₂) [85°] The benzoyl
derivative [167°] is formed, together with that of di nitro di tolyl amine [191°], by nitrating benzoyl di p tolyl amine (Lellmann, B 15,

Hexa nitro di p tolyl amine $NH(C_1HMe(NO_2)_3)_2$ [258°] H Formed from ditolyl-nitrosamine and fuming HNO_s (Lehne, B 13, 1545) Trimetric crystals

NITRO TOLYL-ISOBUTYRIC ACID

[139°] [1 3 6] C_sH₃Me(NO₂) CH₂ CHMe CO₂H [139°] Formed from 10do 1sobutyl toluene and dilute HNO, (S G 1 12) at 200° (Effront, B 17, 2326) colourless plates

NITRO TOLYLENE DIAMINE $C_1H_2N_3O_2$ ie $C_6H_2Me(NO_2)(NH_2)_2$ [1 x 2 6] [154°] Obtained from its acetyl derivative [253°], which is got by nitrating di acetyl tolylene diamine (Tiemann, B 3, 9, Ladenburg, B 8, 1211) Needles, with violet reflex Yields a di-benzoyl de rivative [245°] (Ruhemann, B 14, 2656)

Nitro-tolylene diamine Bensoyl deriva-\$100 CoH2Me(NO2)(NH2)(NHBz)[1 2 5 4] [139°].

Formed by reducing benzoyl-di-nitro-toluidine Hubner, A 208, 317) Red needles (from water). | 14) (A G Perkin, O. J. 87, 698) Needles (from water).

Nitro tolylene diamine C.H. Me(NO2)(NH2); [1 6 4 2]? [182°] Formed by reducing (6,4,2,1)-tri-nitro-toluene (Tiemann, B 8, 218) Red prisms (from water)

Tri-nitro-tolylene-diamine

C.Me(NO.), (NH.), [1 2 4 6 3 5] [222°] Formed from C.Me(NO.), Br., and alcoholic NH., (Palmer, B 21, 3501) Small yellow prisms
NITEO-TOLYLENE-TETRA-METHYL-DI-

AMINE C. H. Me(NO2) (NMe2) [63°] Formed by nitration (Niementowski, B 20, 1888) Prisms

DI-NITRO-DI-TOLYL-ETHYLENE-DIAMINE C.H.(NH C.H.Me NO.). [195°] Formed from (5,1,4) mitro toluidine and ethylene bromide (Gattermann a Hager, B 17, 779) Red plates Formed from NITRO-TOLYL-HYDRAZINE SULPHONIC

 $O_{s}H_{2}Me(NO_{2})(N_{s}H_{3})(SO_{s}H)$ [1 2 4 5] Formed from nitro-p-diaso-toluene sulphonic acid and a cooled solution of SnCl, (Limpricht, B 18, 2194) Tables—BaA', 4aq yellow prisms 18,2194) Tables —BaA', 4aq yellow prisms NITRO-TOLYL-METHYLENE PHTHALIDE B 18, 2194) Tables -BaA'

0=0(NO,) O,H, C,H, [144°] Formed from ∕co∂

tolyl-methylene-phthalide by the action of nitrous $\dot{C}(NO_2)$ CH $(NO_2)C_1H_1$ acid, the resulting CaH. ó OO'

[133°] being boiled with dilute alcohol (Heilmann, 23, 3163) Needles

NITRO TOLYL METHYLENE-PHTHALIM- $C = C(NO_2) C_7H_7$ IDINE C.H. [159°] Formed ·CO NH

from tolyl methylene phthalimidine and nitrous acid (Heilmann, B 23, 8161) Needles (from alcohol)

NITRO m-TOLYL-PROPIONIC ACID C₆H₈Me(NO₂)C₂H₄CO₂H [130°-136°] Formed from (2,5,1) 10do 180butyl toluene and HNO₈ (S G 1 25) at 200° Effront, B 17, 2327) Needles

(from water) DI NITRO DI-TOLYL-PROPIONIC ACID

(C₆H₃MeNO₂)₂CMe CO₂H [129°] Formed. together with the tetra nitro- acid [225°] by ni trating di-tolyl propionic acid (Haiss, B 15, 1476) Yellowish crystals

DI NITRO-DI-O-TOLYL-SULPHAZIDE

C₁₄H₁₄N₁O₆S 2 e [2 4 1] C₄H₂Me(NO₂) NH NH SO₂ C₄H₂(NO₂)Me [1 4 2]? [142°] Obtained by the action of alcoholic SO₂ upon nitro o-diazo toluene (Limpricht, B 20, 1241) Small yellow prisms

NITRO-TOLYL-THIOCARBAMIC ETHER [1 2 4] C₆H₃Me(NO₂) NH CS OEt [96°] Formed by boiling with alcohol nitro-tolyl-thiocarbimide, which is produced by the action of Ac2O on phenyl-nitro tolyl-thio-urea (Steudemann, B 16, Needles, v sol alcohol

NITRO-TOLYL-THIO-UREAS The following compounds have been prepared by Steudemann (B 16, 2867) from C.H.Me(NO.)(NH.) [1 2 4] NH.CS NH C.H.Me(NO.) [1769] [4 1] C.H.Me NH C.H.Me(NO.) [1699]. CS(NH C.H.Me(NO.)). [2079]

DI-NITRO-DI-p-TOLYL-URRA CO(NH C,H₄,NO₂), [c. 288°] Formed from d1-p tolyl-guandine, alcohol, and HNO₂ (S G

NITRO-URACIL V NITRO-DI OXY PY IMIDINE NITRO-URAMIDO-BENZOIC ACIDS three following acids are obtained by boiling the three di-nitro-uramido-benzoic acids with aqueous

NH₂ (Griess, B 5, 193) —

C₄H₄(NO₂)(NH CO NH₂) CO₂H [6 3 1] Crystals,
C₅H₄(NO₂)(NH CO NH₂)CO₂H [4 3 1] Needles,
C₅H₄(NO₂)(NH CO NH₂)CO₂H [2 3 1] Plates

The isomeric C₅H₄(NO₂)(NH CO NH₂)CO₂H[5 3 1] is formed, together with nitro di-uramido benzoio acid, by the action of potassium cyanate on nitro amido benzoic acid (Griess, B 17, 2184) It yields the salt BaA'2 5aq

Nitro-diuramido-benzoic acid

NITRO-UVITIC ACID

(NH2 CO)2N C6H2(NO2)CO2H forms crystals (containing 2aq), and yields the salt BaA', 7 aq Three crystalline di-nitro m-uramido benzoic acids are got by nitrating m uramido benzoic acid A di nitro-p-uramido benzoic acid is formed by nitrating p-uramido-benzoic acid

NITROUS ACID v Nitrogen, p 567. NITROUS ETHER v ETHYL NITRITE

 $C_0H_2Me(NO_2)(CO_2H)_2[1 \times 3 5]$ [227°] Formed, together with an isomeride C,H,NO, 2 aq [250°] by nitrating uvitic acid (Böttinger, B 9, 804, A 189, 171) Prisms (containing 2aq) — $K_{\bullet}A''$ aq needles, m sol hot -BaA" aq —CaA" 3aq water

NITRO VALERIC ACID C4H8(NO2) CO2H Formed by the action of nitric acid on isovaleric acid and on di isoamyl ketone (Dessaignes, A 79, 374, Bredt, B 15, 2319, Brazier a Gossleth, A 75, 262, Schmidt, B 5, 602) Monoclinic AgA' des AgA' prisms (from hot water)
DI NITRO VINYL FURFURANE

C₄H₂(NO₂)O CH CH NO₂. [144°] Formed by nitrating vinyl furfurane (Priebs, B 18, 1362) Yellow needles Yields a dibromide [111]

NITRO VINYL PHENOL Methyl der- $C_6H_s(NO_2)(CH\ CH\ NO_2)OMe[3\ 1\ 4]$ vative [163°] Formed from the methyl derivative of p coumaric acid and HNO₃ (Einhorn a Grabfield, A 243, 369) Yellow needles (from alcohol)

o NITRO-o XYLENE C.H.Me2(NO2) [1 2 4] d w 151 [29°] (258°) S G 30 1 139 8 G 👸 1 139 Mol w 151 [29°] Formed by nitration of o xylene (Jacobsen, B. Long yellow prisms

c-Nitro-o-xylene C_eH₃Me₂(NO₂)[1 2 3] i V at 739 mm) SG 15 1 147 Formed, together with the preceding isomeride, by the action of H2SO, and HNO, on o xylene (Nölting a Forel, B 18, 2669) Liquid

c Nitro-m-xylene $C_0H_2Me_2(NO_2)[1 \ 3 \ 2]$ (225°) at 745 mm S G 15 1 112 Formed from nitro xylidine [78°] by eliminating NH, (Grevingk, B 17, 2430), and, together with the (1,3,4) isomeride, by nitration of m xylene with HNO, and H,SO, at 0° (N a F) Liquid 1-Nitro-m-xylene C,H,Me,(NO,) [1 3 4] (244°

cor) SV 1645 Formed by nitrating m-xylene (Harmsen, B 13, 1558) or its dihydride (Wallach, A 258, 830), and by eliminating NH, from nitro-zylidine [128°] (G) Inquid s-Nitro-m-zylene C,H,Me,(NO) [1 8 5].

[75°]. (263° LV) at 789 mm. Formed by eliminating NH, from intro-xylidine [70°] (Wroblewsky, 4 207, 94, Bl [2] 84, 882, Thöl,

B. 18, 360, Nölting a Forel, B 18, 2678) Needles, volatile with steam

Nitro p-xylene C₂H₂Me₂(NO₂) [1 4 2] (239° 1 V) at 789 mm S G 15 1 132. Formed by nitration of p-xylene (Jannasch, A. 176, 55, NaF) Liquid.

w-Nitro m-xylene C,H,Me(CH,NO,). Formed by the action of alkalis followed by HCl2 on

 $C = C(NO_2) C_6 H_4 Me$ C_0H_0 (Heilmann, B \co`o

3164)

Oil, with irritating odour attro m xylene C₆H₂Me₂(NO₂), [1 3 4 2] Di-nitro m xylene Mol w 196 [82°] Formed, together with the isomeride [93°], by nitrating m xylene with HNO. and H2SO, at 5° (Grevingk, B 17, 2422) Plates, v sol alcohol

Di nitro m-xylene C.H.Me.(NO2), [1346] [93°] Formed by nitrating m-xylene or its di-hydride (Luhmann, A 144, 274, Fittig, A 148, Wallach, A 258, 332) Crystals (from alcohol)

Di-nitro-p-xylene $C_4H_2Me_2(NO_2)_2[1423]$ Formed, together with the isomeride [124°], by nitrating p-xylene (Rammer, Bl [2] 9, 434, Fittig, A 136, 307, 147, 17, Jannasch, A 171, 79, Nölting, B 19, 144, Lellmann, A 228, 252) Monochnic crystals Yields xylylenediamine [75°]

Di nitro p-xylene $O_{e}H_{2}Me_{2}(NO_{e}), [1 4 2 6]$

[124°] Needles

Di-nitro p-xylene $C_6H_2Me_2(NO_2)_2[1425]_2$ Formed in small quantity by nitrating p xylene (L) Long yellow needles (from alcohol)

Tri nitro-m xylene $C_6HMe_2(NO_2)$, [1 3 2 4 6]. Mol w 241 [c 182°] Formed by nitration of m xylene or its dihydride (Luhmann, Grevingk, Tilden, C J 45, 416, Wallach, A 258, 333) Crystals, insol hot alcohol

Tri nitro-p xylene C.HMe.(NO2), [1 4 2 3 5] [140°] Formed by nitration of p xylene (Fittig, Nölting, B 19, 145). Crystals (from benzene)

NITRO m-XYLENE PHOSPHONIC ACID C₆H₂Me₂(NO₂)PO(OH)₂. Two acids of this formula, [100°] and [182°], are formed by nitrating m-xylene (a)-phosphonic acid (Weller, B 20, 1722, 21, 1492) From m sylene (β) phosphonic acid an isomeric acid [107°] is obtained, and another isomeride [224°] may be obtained from p xylene phosphonic acid

NITRO m-XYLENE SULPHONIC ACID

 $C_nH_2Me_2(NO_2)(SO_2H)$ [1 3 6 4] [132°] Formed by sulphonating nitro m xylene and by nitrating m-xylene (a) sulphonic acid (Harmsen, B 13, 1558, Limpricht, B 18, 2191, Claus a Schmidt, B 19, 1418) Crystals NaA'aq—NaA'2aq KA'—NH,A'—BaA'28aq—CaA',6aq S 6 18° - MgA', 9aq - CuA', 6aq - PbA', 4aq AgA' aq

Amide [179°] (L); [187°] (C a. 8) Chloride [98°] (L)

Nitro-m-xylene sulphonic acid

C₆H₂Me₂(NO₂)(SO₂H) [1 3 5 4] [100°] Formed, with the preceding and succeeding and, by nitrating (1,3,4) xylene sulphonic and (C a S) Plates — KA'.—NaA'aq —BaA'alaqa,—CaA',6aq -PbA', aq --CuA', 6aq --AgA' aq. sol. water

Amide [108°] Needles. Chloride [97°]

Nitro-m-xylene sulphonic acid C₆H₂Me₂(NO₂)SO₃H [1 3 2 4] [144°] Formed as above (O a S) Plates (containing aq) —

KA'laq — NaA'aq — BaA', — CaA', — PbA', —

CuA', 2aq — AgA' laq

Chloride [96°] Needles.

Amide [172°] Needles.

Di-nitro-xylene sulphonic acid C₆HMe₂(NO₂)₂SO₃H[1 8 6 5 4] [70°] Formed, as well as the following isomeride, by nitrating m-xylene sulphonic acid (Claus a Schmidt, B. 19, 1425) Plates.—KA'—NaA'aq—BaA', aq. - BaA', 21aq - CaA', 5aq - PbA', 41aq -OuA', 4aq pale green plates

Ohloride [118°] Crystals. Amide [158°] Needles

D1-n1tro-xylene sulphonic acid C₂HMe₂(NO₂)₂SO₂H [1 3 6 2 4] Needles (containing 2aq) (Limpricht, B 18, 2192, C. a. S).
— NaA'qq — KA' — BaA'₂3aq — CaA'₂3²aq —

CuA', 2 aq — PhA', 3 aq prisms.

Chloride [123°] Prisms

Amide [193°] Prisms

C.H.NO. Formed NITRO - m - XYLENOL $C_2H_2Me_2(NO_2)(OH)[1 \ 3 \ x \ 4]$ [68 5° by nitrating m-xylenol (Lako, A 1
Needles — KA' 3aq dark red plates
Nitro m xylenol C_cH₂Me₂(NO₂)(OH) 182, 32)

Formed by the action of nitrous acid on the nitro xylidine obtained by partial reduction of di nitro m xylene (Pfaff, B 16, 616, 1136)

Needles — KA'2aq red crystals

Methyl ether MeA' [57°] Needles

(a) Nitro p-xylenol C₆H,Me₂(NO₂)(OH) [1 4 6 3] [115°] (O), [122°] (G a S) Formed by oxidising nitroso-p-xylenol (the oxim of phlorone) with alkaline K.FeCy. (Oliveri, G 12, 162, Goldschmidt a Schmid, B. Needles, sol. hot water

C.H.Me,(NO2)(OH). (β) -Nitro p-xylenol (236°) Formed by nitrating p xylenol (O).

Oil —BaA'₂ purple scales
(γ)-Nitro p-xylenol [89°] Formed by heating p xylenol sulphonic acid with fuming HNO. (O) Light-yellow scales - KA' aq - BaA', aq. light yellow scales

Nitro-p-xylenol C.H.Me.(NO.)(OH) [1 4 3 5]. [91°] Formed by the action of nitrous acid on the corresponding nitro xylidine (Von Kostanecki, B 19, 2320) Buff-coloured plates; Buff-coloured plates; perhaps identical with the preceding isomeride.

Nitro-p-xylenol Ethyl ether
[85°] Formed from p- $C_eH_2Me_2(\tilde{N}O_2)(OEt)$ xylidine by nitration and treatment with nitrous acid (Nölting, Witt, a. Forel, B 18, 2667)

Di-nitro-o-xylenol C_eHMe₂(NO₂)₂(OH)[1 2 3 5 4] [128°] Formed as a by-product by nitrating o-xylene (Nölting a. Pick, B 21, 3158) Obtained also from (1, 2, 4)-xylidine. Needles, al. sol. cold water

Di-nitro-o-xylenol $C_eHMe_2(NO_2)_2(OH)[1 2 3 4.6]$ [82°] Obtained by nitrating and diazotising (1, 2, 3)-xylidine (N.

s. P.) Orange yellow needles, m. sol water
Di-nitro-p-xylenol [121°] Formed from pxylenol, H.SO., and HNO. (Kostanecki, B 19,
2821) Yellow plates (from water)
MITRO-MAYLENOL SULPHONIC ACID

 $C_0HMe_2(NO_2)(OH)(SO_3H)[1 8.x 6 4]$ from nitro-xylidine sulphonic acid by the diazo reaction (Limpricht a. Sartig, B. 18, 2190, A. 130, 340) -BaA', 3aq -PbA', 3aq The ethyl lerivative forms C.HMe2(NO2)(OEt)(SO3K) aq,

rystallising in plates

NITRO - m - XYLIDINE $C_8H_{10}N_2O_2$ is e [76°] Formed $J_{e}H_{2}Me_{2}(NO_{2})(NH_{2})[1\ 3\ 5\ 4]$ rom acetyl m-xylidine by nitration and saponi ication (Wroblewsky, A 207, 91, Nölting a Forel, B 18, 2677) Orange needles

Acetyl derivative [173°] Needles Nitro-m-xylidine

 $J_{a}H_{2}Me_{2}(NO_{2})(NH_{2})[1\ 3\ 6\ 4]$ [123°] Formed by reduction of di nitro m xylene (Fittig, A 147, 18, Wallach, A 258, 332) and by nitration of 1,3,4) m xylidine (1 pt) dissolved in H₂SO₄ 10 pts) (Nölting a Collin, B 17, 265) Orange needles —B'HCl —B'₂H₂SO₄ —B'₂H₂C₂O₄

Acetyl derivative [160°]

Diacetyl derivative [116°].

Nitro-s m-xylidine $D_0H_2Me_2(NO_2)(NH_2)[1 \ 3 \ 4 \ 5]$ [54°] Formed by nitration of s m-xylidine dissolved in 10 pts of sone H.SO. (Nölting a Forel, B 18, 2679) Yellow needles Volatile with steam

Nitro-m xylidine $\mathbf{O_6H_2}(\mathbf{CH_3})_2(\mathbf{NO_2})(\mathbf{NH_2})$ [1 3 2 4] or [1 3 4 2] [78°] Formed by reduction of di-nitro m xylene [82°] with alcoholic ammonium sulphide (Grevingk, B 17, 2425) Yellow needles, sol hot water

Acetyl derivative [149°] White needles

Nitro p-xylidine $C_6H_2Me_2(NO_2)(NH_2)[1 4 5 2]$ [142°] Formed by nitration of acetyl p xylidine and saponification, or by nitration of \bar{p} xylidine dissolved in conc H2SO4 (Nolting, Witt, a Forel, B 18, 2666) Formed also by reducing di nitro p-xylene (Kostanecki, B 19, 2318) Brownish yellow crystals On reduction it gives the para **dia**mine [147°]

[166°] Acetyl derivative Needles Nitro p xylidine C₆H₂Me₂(NO₂)(NH₂)[1 4 3 5] Formed by reduction of di nitro p xylene [123°] (Fittig, A 147, 22, Kostanecki, B 19, 2320) Needles (from alcohol)

Acetyl derivative [180°] Needles

Di-nitro p xylidine $C_8HMe_2(NO_2)_2(NH_2)$ [1 4 3.5 2] [203°] Formed from tri nitro-p xylene and alcoholic NH₃ (Nölting, B 19, 145) Needles (from HOAc)

Di nitro-xylidine [192°] Formed by reduc tion of tri nitro-xylene (Bussenius a Eisenstuck, A 113, 165, Beilstein, A 133, 45) Yellow needles

NITRO XYLIDINE SULPHONIC ACID

 $C_6HMe_2(NO_2)(NH_2)SO_8H[13x64]$ S 0818 at 8° Formed by intrating xylidine sulphonic acid (Limpricht a Sartig, B 18, 2189, A 230, Needles — KA' $1\frac{1}{2}$ aq — BaA'₂ $1\frac{1}{2}$ aq -

PbA', aq yellow sılky needles NITEO-XYLYLENE DIAMINE C, H,1, N,O,2 v e C_eHMe₂(NO₂)(NH₂)₂ [215°] Formed by reducing tri-nitro-m xylene (Bussenius a Eisenstuck, A 118, 159, Fittig, A 148, 6, Wallach, A 258, 338) Red prisms With EtI at 105° it yields orystalline C₈HMe₂(NO₂)(Net₂)(NHEt) —B"HCl —B"H₂Cl₂ — B"H₂PtCl₃ 3aq — B"H₂SO₄ 2aq — B"(H₂SO₄), 2aq —B"₂H₂SO₄ NITEYL CHLORIDE v Netrogen oxychlor-

NOBLE METALS The elements Gold, Ruthenrum, Rhodrum, Palladrum, Iridrum, Osmum, and Platinum are sometimes classed

together as the noble metals. The application of the term noble to metals is a survival of the alchemical notion of a close connexion between physical and moral properties Gold was regarded by the alchemists as the purest metal, as that which most nearly approached their ideal ele ment As gold did not change when heated in air, and did not dissolve in any single acid, these two properties came to be looked on as character istic, and when these properties were found to belong also to certain other metals these other metals were placed in the same class as gold Silver dissolves in nitric acid, but it does not change by heating in air, hence Ag was often classed with Au as a noble metal The term noble is applied in this article to the seven metals named above, as a convenient form of expressing the fact that these metals have many properties in common The seven metals are all found un combined in nature, they are all very lustrous, heavy, generally ductile and malleable, haid (except Au), some are not oxidised by heating in air, others combine with O at high tempe ratures

Au has been known from prehistoric times Pt was discovered about 1750, and the other Pt metals from 1803 to 1845 The name platinum is said to be derived from platina del Pinto (platina = diminutive of plata = silver), a name by which the natural alloy of the metal was known in New Granada, from whence it was first obtained The names palladium and rho dium were given by Wollaston who separated these metals from Pt ore, in 1803, the first sug gested by the planet Pallas discovered about that time, and the second from posov = a rose, in allusion to the colour of solutions of the salts of the metal Tennant discovered two other metals in Pt ore, in 1803, he called one iridium, be cause of its many coloured salts (lpis = the rain bow), and the other osmium, because of the peculiar smell of its volatile oxide $(o\sigma\mu\dot{\eta} = a$ smell) In 1845, Claus separated a sixth metal from Pt ore from the Ural, and called it ruthe nium, in allusion to Russia

Ru, Rh, Pd, and Ir, Os, Pt, form the second and third sections or families of Group VIII in the periodic classification of the elements, the first family of this group is composed of Fe, Ni, Au belongs to Group I, it is a mem he family Cu, Ag, Au As Cu follows and Co ber of the family Cu, Ag, Au immediately after Fe, Ni, Co in the long period beginning with K and ending with Br, and as Ag follows Ru, Rh, Pd, in the long period Rb to I, so Au is placed in immediate succession to Os, Ir, Pt in the long period which, when it is complete, will begin with an alkali metal re sembling Cs and end with a halogen more or less lıke I Looking at the position of Au in the periodic scheme of classification (v Table, p. 204, vol 11) one may say that the relations of this element to Os, Ir, and Pt will be found very simi lar to the relations of Ag to Ru, Rh, and Pd, and also to the relations of Cu to Fe, Ni, and Co

The table on page 629 presents some of the important properties of the metals Ru, Rh, and

These three metals form oxides MO and MO, Ru and Rh also form M₂O₃, Ru forms a volatile oxide RuO₄, Rh forms RhO₃, and Pd₂O is known The oxides MO are basic, forming salts

	BUTHENIUM	RHODIUM	PALLADIUM
Atomic weights		102 7 se elements which has been ined directly Molecular we	
Spec gravities (approx)	128	121	114
Atomic weight spec gravity	85	86	98
Melting points (approx)	above 2000°	2000°	1500°-160 0°
Spec heats	061	058	06
Occurrence and preparation	The metals Rh, Ru, and Pd, occur in small quantities in many Pt ores, they are usually separated in the form 2NH ₄ Cl MCl ₄ , on strongly heating these double chlorides, the metals remain		
Physical properties	brittle, crystalline, less	Greyish white, very hard, malleable, not very duc tile, may be fused in O H flame, and is thus obtained in crystals	ductile and malleable, most fusible of the Pt
Chemical properties	Oxidised by heating pow dered metal in air, also by heating with KOH or K_CO ₃ , forming K_RuO ₄ which is sol water Combines with Cl at red heat, dissolves very slowly in aqua regia	heat, unacted on by any acid, but when alloyed	

 $MX(X = SO_4 dc)$ Ru₂O₃ and Rh₂O₃ are also A few basic, the corresponding salts are M 3X salts corresponding with RuO have been isolated, but none derivable from RhO2 or PdO2 has been prepared RhO, has not yet been proved to be basic RuO, is not known, but a few salts (ruthenates) have been isolated in which RuO, forms the negative radicle, e g K.RuO. An scid HRuO, is known, the K salt (KRuO.) is said to be isomorphous with KClO, and KMnO, RuO, is a solid melting at c 26°, it is very volatile, easily reduced to lower oxides, explodes at c 108° giving RuO, and O, with KOHAq it forms K RuO, The chlorides generally correspond with the oxides MO, M2O3, and MO2, the chlorides form double chlorides with more positive chlorides, the salts MCl, 2XCl are best regarded as salts of the acids H₂MCl_s (e.g. K₂PdCl_s and (NH₄)₂RuCl_s) The cyanides MCy₂ form double salts, an acid H₄RuCy₅ is known The sulphides generally correspond with the oxides MO, M2O1, and MO2, PdS, forms thio-salts, Na,PdS, &c; Rh, S, dissolves in alkali sulphides the sulphides M2S, and MS, are therefore more or less acidic The three metals form many ammoniacal compounds, which are best regarded as salts of various radicles obtained by replacing H in two or more NH, molecules by Ru, Rh, or Pd

In the table on page 680 are presented some of the more important properties of the metals Os, Ir, Pt, and Au.

Au differs considerably in its chemical properties from Os, Ir, and Pt The oxides of Os, Ir, and Pt are MO and MO₂, M₂O₃, represented by Os₂O₃ and Ir₂O₃, OsO₄ Very few salts of Os by Os₂O₃ and Ir₂O₃, OsO₄. Very few salts of Os have been prepared as yet, OsO and Os₂O₃ are probably basic OsO, is not known, but osmates, cg K2OsO4, have been isolated OsO4 is solid, with low melting and boiling points, it is slowly soluble in water, seems to form very unstable salts with alkalis, but does not decompose carbonates Os forms a peculiar acid H2N2Os2O6, perhaps HO OsO, N N OsO, OH, it also forms ammoniacal bases, in which OsO seems to re place H₂ in N₂H₈, and OsO₂ to replace H₄ in N₄H₁₆ The acid H₄OsCy₆ is known Very few salts of Ir are known, Ir,O, is basic chloride IrCl, corresponding to IrO2, is known, and also such salts as IrO SO₃, in which an acid radicle seems to replace O in IrO₂ Some indates have been obtained, e.g. K₂O 2IrO₃. The acid HaIrCy, and salts of this acid, exist Some ammoniacal bases are known, in which Ir seems to replace H2 of N2H2 A few salts corresponding with PtO are known, but they have been but little studied, PtO₂ forms salts such as Pt(SO₄)₂ PtO₂ also combines with some positive oxides to form salts xPtO₂ yRO, e.g. PtO, also combines with acidic 3PtO2.Na2O and basic oxides to form complex salts, e.g. PtO₂.10MoO₃(or10WO₃) 4Na₂O xH₂O. A very large number of salts of complex ammoniacal

	Ояміим	Īridium	PLATINUM	Gorp
Atomic weights	190 3	192 5	194 3	19/
	The only compoun S H of each has	sified is OsO ₄ The eights are unknown.		
Spec. gravities (approx)	22 5	22 4	214	19 5
Atomic weight Spec gravity	85	86	9	10 1
Melting points (approx)	Melts in the electric arc	1900°	1800°	, 1200°
Spec. heats	0311	0326	0324	0324
Occurrence and preparation	associated (? allog with Ru, Rh, and	yed) with each oth Pd They are us	nn small quantities, ier, and frequently smally separated as congly heating these	Occurs native, generally alloyed with Ag Prepared by removing earthy impurities, or by crushing aurifer ous quartz, forming an amalgam of Au and Hg, and removing Hg by heat, sometimes by smelting, or by treatment with Ol &c
Physical properties	White, with tinge of blue, very hard, crystalline, brittle, also a black, amorphous, powder Os does not melt at the highest temp of the O-H flame, it is the heaviest substance known	White, lustrous, hard, orystalline, brittle, but fairly malleable at red heat, also a hard black powder Melts in O H flame	hard, very malle- able and ductile, expands by heat less than any	yellow metal, crystallises in octahedra, good
Chemical properties	Oxidised readily, to OsO., by heating finely powdered metal in air, also oxidised by HNO., when in fine powder Oxidised by fusion with KOH or KNO. Combines directly with Cl	vided, oxidises slowly when heated in air, and dissolves in aqua regra, in compact form is insol in allacids Oxidised by fusion with	O, but by fusion with KOH Dissolves in aqua rega Combines directly with Cl Absorbs H rapidly, and gives it off again at red heat	Not oxidised by heating in air Dissolves in aqua regia Combines directly with Cl, Br, and I Com pounds are easily decomposed, yield

bases, containing Pt, are known Pt is rather remarkable for the number of compounds which it forms with H and acidic radicles, these compounds are acids, and corresponding with each is a series of salts; the acids in question are H_PtGl, H_PtGl, H_PtGl, H_PtGl, H_PtGl, H_PtGl, Gl, H_PtGl, Galts of H_Pt_S_e exist)

Au forms three oxides, Au₂O, AuO, and Au₂O₃, Au₂O is slightly sol cold water, a few salts corresponding with Au₂O₃ are known, e.g. Au(NO₃)₃, AuSO₄ corresponds with AuO Au₂O₃ forms aurates. A₂ KAnO₋ by reacting with pounds are acids, and corresponding with each

but these thio salts have been examined very slightly The chlorides are AuCl and AuCl., the acids HAuCl, HAuBr, and HAuCy, and salts of the form M'AuI, are known The compounds of Au are easily decomposed with separation of Au

The Pt metals fall into two families. (1) Ru, Rh, Pd, and (2) Os, Ir, Pt The elements, as a group, possess the physical characters of metals very distinctly marked, but the existence of acidic oxides and sulphides points to the nonmetallic nature of these elements Au is physiforms aurates, e.g KAnO₂, by reacting with cally more metallic, and chemically more non-alkalis. The sulphides, Au₂S and AuS, form metallic, than any of the other noble metals. this salts with the alkali sulphides, e.g NaAuS, For the relations of Au to Cu and Ag, and the relations o this family to the members of Group VIII (Fe, Ni, Co, Ru, Rh, Pd, Os, Ir, Pt), and also to the other members of Group I (Li, Na, K, Rb, Cs), v Copper group of elements, vol., i p 250, v also Iron group of elements, this vol p 65 For details about the individual noble metals, v Gold, vol 11 p 647, Iridium, this vol p 46, Osmium, Palladrium, in this vol, Platinum, Rhodium, and Ruthenium in vol 1v.

M M P M

NOMENCLATURE The nomenclature of chemistry is based on the system introduced by Lavoisier, De Morveau, Berthollet, and De Four-croy in 1787 The leading principles laid down by the French chemists were (1) that every substance is to be regarded as an element until it is proved to be otherwise, (2) that the name of a compound is to exhibit the elements, and as far as possible the relative proportions of the elements, of which it is composed The names given to elements are not based on any uniform principle, some are known by the names given them for centuries, more recently discovered elements are named, sometimes from the names of compounds of them well known before the elements were discovered, sometimes from the localities where the material was found from which the element was prepared for the first time, sometimes from a characteristic property of the element, sometimes from fanciful considerations, and sometimes to express the pride of the discoverer in his own nationality To all more recently discovered metals have been given names ending in um Binary compounds are designated by names ending in ide, this termina tion being applied to the name of the more negative element, thus all binary compounds of O are called oxides As Cl is more negative than S, it is better to call S₂Ol₂ sulphur chloride than chlorine sulphide When two oxides, chlorides, &c, of an element exist, they are generally dis tinguished by throwing the name of the more positive element into adjectival form, and using the termination to to indicate more of the negative element, and ous to denote less of the nega tive element, relatively to a fixed quantity of the more positive element, thus the compounds FeCl. and FeCl, are known as ferrous chloride and ferrio chloride respectively When more than two oxides, chlorides, &c, of an element are known, it is customary either to use prefixes di- (or bi), tri- (or ter), &c , or to indicate the relative proportions of the elements by such prefixes as hypo and per It is also customary to give names to certain oxides for the purpose of in-dicating their acidic character Thus the five oxides of N have been named as follows at different times

N₂O Nitrous oxide, nitrogen monoxide (might also be called hyponitrous anhydride)

NO Nitric oxide, nitrogen dioxide

N₂O₃ Nitrogen trioxide, nitrogen sesquioxide, nitrous anhydride

N₂O₄ Nitrogen dioxide, nitrogen tetroxide, nitroso-nitric anhydride, nitrogen peroxide

N₂O₅ Nitrogen pentoxide, nitric anhydride, nitrogen peroxide

The same name—nitrogen dioxide—has been given to two different compounds, NO and NO;

and the name peroxide has been used for NO. and N₂O₅ This illustrates a difficulty The prefixes mono, di-, &c. are sometimes employed to designate the first, second, third, &c, members of a series of oxides, chlorides, &c of the same element, without implying anything as to the number of O, Cl, &c atoms in the molecules of the various compounds, but the same prefixes are employed sometimes to imply one, two, &c atoms of O, Cl, &c On both systems of naming N₂O is called monoxide, on the first system NO is called dioxide, but on the second system it must be called monoxide, hence the second system of naming gives the same name to two To get over this difficulty different compounds N₂O may be called dinitrogen monoxide, and NO mononitrogen monoxide, but such names are cumbersome The prefix per- 18 generally employed to designate the highest compound of a series, te the one with relatively most negative element, but a higher compound may be dis covered, in such a case the prefix, if used at all, must be moved from the older to the more recently discovered substance Salts are named from the acids of which they are metallic de rivatives If there are two acids containing the same elements, to that with relatively more of the negative radicle is given a name ending in -ic, and its salts are called -ates, to the other acid is given a name ending in ous, and its salts are called ites By the use of prefixes per, hypo, &c, four or five acids and their salts may be named, e q

HClO Hypochlorous acid.
HClO Chlorous acid
HClO Chloric acid
HClO Perchloric acid

Compounds which probably contain the OH group are generally called hydroxides, and those containing the SH group are called hydro sulphides or sulphydrates These names more or less imply a special view of the structure of the compounds, as the same view is not always held by all chemists, it seems preferable to call a commonly occurring compound, such as KOH, potash, rather than potassium hydroxide The nomenclature of organic chemistry must be based on certain conceptions regarding the structure of carbon compounds These compounds are so numerous, and many of them show such small differences in empirical com position, while not a few are identical in com position, that it would be impossible to frame a systematic nomenclature without the help of the conceptions of molecular structure which lie at the root of organic chemistry In other words names cannot be found for the vast variety of carbon compounds without considering the properties and functions of these compounds as wel as their composition, but the only way we have o expressing, at present, the chemical properties of carbon compounds is in terms of the mole cular and atomic theory For complicated ex amples v Azo- compounds, vol 1 p 369, to some simpler cases v Hydrocarbons, vol. 11 p

No attempt is made in this article to trace the historical development of chemical nomen clature, nor to discuss fully the present system of naming used in the science Chemical nomen clature is a subject the details of which must b tearned gradually by studying chemical substances and their reactions The article Nomen-CLATURE in the first edition of this Dictionary contains references to the more important older memoirs on the subject. In addition to these should be added a report on chemical nomenclature by a committee of the British Association (B A 1884 39) Reference should also be made to the suggestions of the Council of the Chemical Society (C J 35, 277) MMPM

NONADECANE v ENNDECANE

NONANE v ENNANE

NONAPHTHENE C.H. (136° cor) S G 20 763 H C v 1,380,900 H C p 1,383,400 Occurs in Russian petroleum (Markownikoff, J R 15, 331, Ossipoff, J R 20, 645) It is ψ cumene hexahydride as it yields \(\psi \) cumene sulphonic acid on treatment with H₂SO₄ (Konovaloff, C C 1887, 1183, J R 22, 4, 118) Br and AlBr, yield tri bromo ψ cumene Nitric acid (S G 14) yields C₈H₁₈NO₂ (219°), which on reduction yields C₈H₁₈NH₂ (172°-177°), S G ² 873, smelling like confine Chlorine yields C,H1,Cl (186°), ing like conline Chlorine yields C_9H_1 , C_1 (100 f_1), whence C_9H_1 , $(110^\circ$ at 200 mm), C_9H_1 , OAc (209°), and C_9H_1 , OH (191°), $SG \frac{20}{20}$ 8972 may be successively derived Nonaphthyl iodide is converted by Ag, O into (C_9H_1) , O (301°), $SG \frac{20}{20}$ 866 Nonaphthylene C_9H_1 s (136°), $SG \stackrel{1}{2}$ 807 may be obtained from penephthyl chloride may be obtained from nonaphthyl chloride

Isononaphthene C_9H_{18} (151°) H C v 1,381,700 H C p 1,384,200 Occurs also in Rus-

sian petroleum

NONIC ACID C₁₀H₁₆O₂ [187°] Formed by the action of bromine and alcoholic potash on 180propyl 180valeric acid (Wohlbruck, B 20, 2336) Plates

NONOIC ACID v ENNOIC ACID

NONYL The radicle C9H19, called ENNYL in this Dictionary

Di-nonyl 18 OCTODECANE

NONYL ALCOHOL v ENNYL ALCOHOL

NONYLENE v ENNYLENE

NONYLENIC ACID v ENNENOIC ACID

NONYLIC ACID v ENNOIC ACID

NORMETHYLHEMIPIC ACID v Methyl de rivative of DI OXY-PHTHALIC ACID

NORMETHYLNITROHEMIPIC ACID Methyl derivative of Nitro di oxy phthalic acid

NORNARCOTINE v NARCOTINE

NOROPIANIC ACID v OPIANIC ACID

NORWEGIUM Ng (?) At w c 219 This name was given by Dahil to a substance separated by him from nickel glance from the Norwegian island of Ostero and ranked by him among the elements (B 12, 1781, 18, 250) According to Prochazka (A C J 2, 213) the ele ment exists in some specimens of unrefined Pb (along with Bi, Cu, and Ni) The claim of Ng to rank as an element cannot be regarded as yet satisfactorily established Ng is said to show great resemblances to B1, to melt at c 254°, to form a fusible oxide resembling Bi₂O₃. The hydroxide is soluble in KOHAq, also in a large excess of NH, or Na carbonate solution If the oxide is Ng₂O₂, the at w is approximately 219, if the oxide is NgO, the at w is approximately MMPM

NOTATION The expression of the composition, and, as far as possible, the properties, of compounds by the use of symbols and formulæ The subject is discussed sufficiently in the articles Equations, chemical (q v vol 11 p 433), Formulæ (q v vol 11 p 572), and Isomerism MMPM

(q v this vol p 79) NUCIN v JUGIONE

NUCITANNIN Occurs in walnuts (Phipson, C N 20, 116) Decomposed by dilute acid into sugar and red amorphous rufic acid C14H12O1, which yields the salts CaC H24O15 and PbC_{1,}H₁O₈
NUCLEIN v PROTEIDS, Appendix C

NUCLEO ALBUMIN v PROTEIDS, Appen-

NUCLEO PROTEÏDS v PROTFIDS, Appen dix C

NUMBERS, LAW OF EVEN Laurent (A Ch [3] 18, 266) said that the sum of the mono valent, trivalent, and pentavalent elements con tained in any well defined and stable compound is always an even number This law of even numbers was long an article of belief among orthodox chemists If by an n valent element is meant one the atom of which combines directly with n other atoms to form a molecule, then there are several exceptions to the so called law, egthe molecules InCl2, InCl2, and probably InCl exist as gases, so do the molecules FeCl₂ and FeCl₃, the molecules WCl₄, and WCl₄, &c M M P M

molecules WCl, and WCl₆, &c
NUPHARIN C₁₈H₂₄N₂O₂ An amorphous substance in the rhizome of Nuphar luteum

(Gruning, J 1882, 1156) NUX VOMICA v STRYCHNINE

O

n-OCTADECANE C16H38. [28°] (317°). S G 29 775, 49 768 Occurs in paraffin from brown coal Formed by reduction of steams acid with HI and P and by the action of Na on ennyl iodide (Krafft, B 15, 1703, 16, 1723, 19, 2221, 21, 2261) Hexagonal tables

OCTADECINENE C., H4 [80°] (184° at 15 mm) SG 20 8016 Formed by heating C., H4, Br, with alcoholic potash (Krafit, B 17, 1374). Plates.

OCTADECOIC ACID (C_sH₁,)₂CH CO₂H [89°] (above 300°) Prepared by heating di octylmalonic acid (Conrad a Bischoff, B 13, 597). White crystals

OCTADECYL ALCOHOL C,H,OH [59°] (210° at 15 mm) S G 7 8048, 7 7849 Occurs in crude cetyl alcohol, and is prepared by reducing stearic aldehyde with zincdust and acetic acid (Krafft, B 16, 1722, 17, 1627).

mm)

OCTA DECYL-BENZENE C18H2, C6H3 (249° at 15 mm) Formed from octadecyl 10dide, iodo benzene, and sodium (Krafft, B 19, 2984) Yields a solid sulphonic acid

OCTADECYLENE $C_{18}H_{26}$ [18°] (179° at 15 mm) S G $\frac{17}{2}$ 7910, $\frac{27}{2}$ 7881 Formed by distilling octadecyl palmitate (Krafft, B 16,

3024)

Octadecylene C18H26 **Anthemene** SG 15 942 VD 127 (H=1) Obtained from Anthemis not lis by extracting the blossoms with ligroin (Naudin, Bl [2] 41, 483) needles

OCTADECYLENE BROMIDE v DI BROMO-OCTADECANE

OCTADECYL IODIDE $C_{18}H_{37}I$ [33 5°] (K), [43°] (S) From the alcohol, I, and P (Krafft, B 19, 2984, Schweizer, Ar Ph [3] 22, 753)

OCTADECYL-PHENOL C18H2, C6H4 OH [84°] (277° at 15 mm) Formed by fusing octadecylbenzene sulphonic acid with potash (Krafft, B

19, 2985) Plates (from alcohol)

n OCTANE C_8H_{16} Mol w 114 (125°) S G 7 7188 V D 4 03 (Lemoine, Bl [2] 41, 163) C E (0°-10°) 001186, (0°-100°) 001331 (Thorpe, C J 37, 217) S V 1863 Occurs in American petroleum (Pelouze a Cahours, A 127, 197, Schorlemmer, C J 15, 419) Formed by the action of zinc and HClAq on sec octyl iodide (Schorlemmer, C J 27, 1029), by the action of sodium amalgam on n octyl iodide (Zincke, A 152, 15), and by the action of sodium on n butyl iodide (Schorlemmer, A 161,280) Obtained also by distilling whale oil under pressure (Engler, \vec{B} 22, 595) Oıl

Iso-octane Pr CH. CH, Pr Di isobutyl (108°) S G 2 709, 20 693 (W), 2 711 (Thorpe) C E $(0^{\circ}-10^{\circ})$ 001205, $(0^{\circ}-100^{\circ})$ 001401 $\mu_{\rm D}=1$ 3943 at 16° (W) R_D = 64 47 S V 184 5 (Schiff, A 220, 88) V D 3 94 Formed by electrolysis of potassium isovalerate (kolbe, A 69, 261, C S Mem, 3, 378, C J 2, 157) Formed also by the action of sodium on isobutyl iodide and on a mixture of isoamyl and isopropyl iodides (Wurtz, A 93, 112, 96 364, Schorlemmer, Pr 16, 37, A 144, 188, W C Williams, C J 31, 541, 35, Occurs also among the products of the distillation of whale oil under pressure (Engler, Oil B 22, 595)

Octane C2Me. Hexa methyl ethane (106°) Formed from tert butyl iodide and sodium

(Lwow, Bl [2] 35, 169)

Octane C.H₁₈ (119°) VD 3.97 (obs) SG 11 712 Formed by reduction of conune, coniceine, or conhydrine by prolonged heating with HI and P (Hofmann, B 18, 12)

OCTANE DICARBOXYLIC ACID C10H18O4. [184°-194°] A product of the action of sodium on bromo methyl ethyl acetic ether (Pagenstecher, A 195, 121) Crystals (from water)

Octane dicarboxylic acid

CO.H CH., CHMe [CH.], CO.H [44°] Methylazelate acid Formed by heating the tetracarboxylic acid (Perkin, jun., C. J 51, 218) Crystals —Ag.A". Ethyl ether Et.A". Oil.

Octane tetracarboxylic ether (CO₂Et)₃CH CHMe (CH₂)₄ CH(CO₂Et)₅. (275° at 60 mm.). A product of the action of di bromo-

Acetyl derivative [c 31°] (223° at 15 | methyl pentamethylene on malonic ether (Perkin. C. J 53, 217) Syrup

Octane tetradeca-carboxylic ether

CO₂Et CH₂ [C(CO₂Et)₂], CH₂ CO₂Et Formed from chloro butane heptacarboxylic ether and sodium butane heptacarboxylic ether (Bischoff, B 21, 2116) Viscid oil

OCTENE v OCTYLENE OCTENOIC ACID C₈H₁O₂ i.e Pr CH₂ CH CH CH₂ CO₂H (231°) Formed by distilling isobutyl paraconic acid (Fittig, B 21,

920, A 255, 103) Orl

Octenoic acids are also formed by oxidation of octenoic aldehyde (Fossek, M 2, 622), and by reduction of suberene carboxylic acid C,H, O, (Spiegel, A 211, 119) They are volatile with

OCTENOIC ALDEHYDE C,H,O (150° at 18 mm) Formed by heating isobutyric aldehyde with conc NaOAcAq at 150° (Fossek, M. 2, 614) Liquid, volatile with steam Forms a mirror with ammoniacal AgNO, and a crystal line compound with NaHSO, Yields acetic and isobutyric acids on oxidation

Octenoic aldehyde PrCH CEt CHO (173°). Formed from butyric aldehyde and aqueous NaOH or NaOAc (Raupenstrauch, M 8, 108) Reacts with phenyl hydrazine Yields C₈H₁₆O (161°) on reduction with iron and HOAc

Octenoic aldehyde CaH,4O (230° 1 V) S G 2 958 Formed by passing dry HCl into 150 butyiic aldehyde (Oeconomides, Bl [2] 36, 209) Oil, resinified by potash Reduces ammoniacal

AgNO, forming a mirror OCTENYL ALCOHOL C.H. O 1 e

Di ethyl allyl carbinol CH CH CH, CEt2OH (156°) SG § 889 CE (0°-33°) 00104. Formed from di ethyl ketone, allyl iodide, and zinc (Schirokoff a Saytzeff, A 196, 113) Oil Lields di ethyl ketone and propionic acid on With HOCl it forms a compound oxidation converted by caustic potash into tm-oxy octane KMnO₄yields CEt₂(OH) CH₂ CO₂H Dilute H SO₄ at 100° yields octinene (c 123°) (Reformatsky at 100° yields octinene (c. 123°) (Reformatsky, J pr [2] 30, 217)

Octenyl alcohol CMePr(C.H.)(OH) (160°). SG & 8486, 20 8345 Formed from methyl propyl ketone, allyl iodide, and zinc (Semljamtzin, J. pr. [2] 23, 263, Reformatsky, J. pr. [2] 40, 412) Yields CMePr(OH) CH₂CO₂H on oxidation

OCTENYL CHLORIDE C₆H₁₃ CH CHCl (168°) SG 2 927 Formed from C. H16Cl and alcoholic potash (Béhal, A Ch [6] 15, 278) Liquid, smelling like carrots

OCTINENE C.H., te CH. C C C.H., Methylamyl-acetylene (133°) 8 G 2 771 Formed by the action of alcoholic potash on octylene bromide (derived from octylene got by dehydrating octyl alcohol) (Rubien, A 142, 299, Béhal, Bl [2] 47, 33, 48, 704, 50, 359, 629, A Ch [6] 15, 274, 428) Mobile liquid Does not react with ammoniacal Cu₂Cl₂. On dissolving in cold H₂SO₄ and pouring into ice-cold water it yields the ketone C₂H₁₆O (171°), SG ² 885 which forms hexoic and acetic acids on oxidation.

Octinene C,H₁, te CH C CH₂,C,H₁₁, (125°-133°) Obtained by heating the preceding isomeride with sodium at 110° (Béhal). Liquid Forms a yellow pp with ammoniacal cuprous

chloride

Octinene C.H.: Conylene (125°) V D 55 6 (H=1). Obtained by dry distillation of dimethyl coniine methylo-hydroxide and by heating 'azoconhydrine' with P.O. (Wertheim, A 123, 170, Holmann, B 14, 710) Oil. Forms a Oil. Forms a di-bromide (v Dr-BROMO-OCTYLENE)

Octinene C.H. Dissocrotyl [5°] (125°-180°) Formed from CMe, CHBr and Sodium (Pribytek, J. R 20,506). Oil, rapidly absorbing

Octunene CH, CMe CH, CH, CMe CH, (114°) Formed from CH, CMe CH, Cl and sodium

(Przybytek, B 20, 3240)

Octunene C₂H₁₄. (c 123°) S G § 7734, <u>E4</u>
7588 R₂, 62 12 Formed by heating octenyl alcohol OH₂ CH CH₂ CEt₂OH with dilute H₂SO₄ at 100° (Reformatsky, J pr [2] 30, 217) Mobile liquid, absorbing oxygen from the air Combines with bromine Oxidised to acetic and propionic acids by chromic acid mixture. Yields C,H,Br,

Isomeride: Xylene tetrahydride OCTINOIC ACID v DI ALLYL ACETIC ACID OCTINYL ALCOHOL C.H.40 ve

(CH, CH CH,) CMe(OH) Methyl-dr-allyl-car-binol (158° cor) S G 8 864, 5 852 H C 1,201,400 (Longuinine, A Ch [5] 23, 388) Formed from allyl iodide, acetic ether, and zinc (Saytzeff a Sorokin, B 9, 33, 277, A 185, 169) Yields oxy-methyl glutaric acid on oxidation

Acetyl derivative (177° cor). OCTODECANE v OCTADECANE

n OCTOIC ACID C₃H₁₀O₂t e CH₂(CH₂)₆ CO₂H
Caprilic acid Mol w 144 [17°] (237° 1 V)
S G ²₀ 927 (Zander, A 224, 71), ¹⁵₁₅ 913, ²⁵₂₅ 908
M M 8 565 at 18 5° S 25 at 100° H C
1,138,694 (Louguinine, A Ch [6] 11, 221),
1,145,600 (Stohmann, J pr [2] 43, 18) C.E
(0°-10°) 00092 S V 197 S Occurs as glyceryl ether in butter (Lerch, A 49, 214) in cocos nut oil (Fehling, A 53, 399, Renesse, A 171, 380), and in Limburg cheese (Illenko, A 55, 85) It occurs also in fusel oil from various sources Formed by oxidation of n octyl alcohol (Zincke, A 152, 9) and by saponifying its nitrile which is formed by the action of bromine and NaOH on the amide of ennoic acid (Hofmann, B 17, 1408) Formed also by oxidising di-oxy stearic acid with alkaline KMnO₄ (Spiridonoff, J pr [2] 40, 248) White crystals, insol cold water

Salts —BaA', S 62 at 20° — CaA', aq —
ZnA', [186°] —PbA', [84°] —CuA', [266°] —
AgA' white curdy pp

Methyl ether MeA' (193°) S G § 8942

8 V 220 1 C.E (0°-10°) 00094 (Gartenmeister, A 233, 286)

Ethyl ether EtA' Mol. $\frac{1}{6}$ 8842 SV 2459. Mol. w 172 (206)O.E ·00098.

S G § 8805.

8 G. 2

**O0098.

**Propyl ether PrA' (225°) SG & SV. 270 S CE (0°-10°) 00092

**Butyl ether O.H.A' (240 5°). Series Sv. 295 S C.E (0°-10°) 00094

**Heptyl ether O.H.A'. (290°) Series Sv. 295 S C.E (0°-10°) 00086

**S754 SV S770 C.E (0°-10°) 00086 SG & n-Octyl ether C.H., A' (806°) 8 8755 SV 404 8. CE (0°-10°) 00084

Phenyl ether PhA'. (300°) Amide C.H.O.NH. [106°]. S. 454 at 100°. Plates.

Anhydride $(C_1H_{12}O)_2O$. (c 285°). (Chiozza, A. 85, 229).

Nitrile C, H, CN. Nitrile C.H. CN. (195°) (F); (199°) (Hofmann, B 17, 1410). SG 13 82 (Felletar, Z [2] 4,665)

Iso-octore acid C₂H₁₆O₂ (219°) S G 2 926; 9911 S 15 at 15° Formed by oxidising isooctyl alcohol (W C Williams, O J 31, 542, 85, 129) Liquid - NaA'.-KA' - MgA'. 2aq - AgA'. Crystallises from hot water

Ethyl ether Eth' (175°).

Iso-octyl ether C₅H₁,A' (c 280°)
Octoic acid CH₂Pr CH₂ CHMe CO₂H (c 215°)
Formed by oxidation of isodibutol C₅H₁₈O (But lerow, A 189, 70) Liquid Probably identical with the preceding acid

Octore acid CMe, CMe, CO2H? (210°-230°) Formed, in small quantity, by passing CO over a mixture of NaOMe and NaOAc at 200° (Geuther a. Fröhlich, A 202, 313)

Octoic acid Pr.CH CO.H

Di n-propyl acetic acid (220°) SG 2 9215 Obtained by boiling di propyl acetoacetic ether with alcoholic potash or by heating di propyl-malonic acid (Burton, Am 3, 389, Furth, M 9, 317)—CaA', 2aq S 957 at 0°, 165 at 80°— BaA', —AgA' S 128

Ethyl ether EtA'

Ethyl ether EtA' (183°)
Octoic acid CH_Pr CMe₂ CO₂H [18°] (215°) Obtained from its ether, which is formed by the action of sodium on isobutyric ether (Brugge mann, A 246, 149) Large hexagonal plates

OCTOIC ALDEHYDE C₂H₁₆O (171°) Occurs among the products of the distillation of castor oil soap (Limpricht, A 93, 242, Bouis, A Ch [3]48, 99, Stadeler, J pr 72, 241, Dachauer, A 106, 270, Béhal, Bl [2] 47, 33, 163) Formed also by distilling a mixture of calcium octoate and calcium formate Liquid Combines with NaHSO. Yields a mirror with ammoniacal AgNO,

Oxim (222°)

Octoic aldehyde C.H.CHEt CHO Formed by reduction of octenoic aldehyde (Rau penstrauch, M 8, 108) Oil Volatile with

steam Reduces ammoniacal AgNO₁
OCTO-ICOSONOIC ALDEHYDE C₂H₃₀O + e
C₄H₁₀CH C(C₄H₁₁) CH C(C₄H₁₁ potash or of Ac₂O on heptoic aldehyde (cenanthol) (Perkin, C J 43, 66) Oil Yields a mixture of heptoic and hexoic acids on fusion with potash

OCTONAPHTHENE C. H. (119°) Occurs in Russian petroleum (Markownikoff, B 20, 1851) Yields a very little tri nitro-m-xylene on treat ment with H₂SO₄ and HNO₅ H₂SO₄ yields a sulphonic acid, the amide of which crystallises ın needles [220°]

OCTYL The radicle C₂H₁₇, which is also called CAPRYL.

Di octyl v Hexadecane

OCTYL ACETATE v Acetyl derivative of OCTYL ALCOHOL

DI-OCTYL-ACETONE v METHYL HEPTADECYL

n-OCTYL ALCOHOL C.H. O. Mol. w 130 (195 5° L.V.). S G 3 8875 (Z); \$\frac{1}{2}\$ 8301, \$\frac{2}{3}\$ 8249 (P). C.E (0°-10°) 00080 MM 8880 at 20° (Perkin) S V 190 6 (Zander, A 224, 84); 197 8 (Ramsay) Obtained from its acetyl derivative which occurs in the volatile oil of cow

paranep (Heracleum Sphondyleum), and in the oil of H giganteum (Zincke, A 152, 1, B. 4, 822, Möslinger, A. 185, 26) The butynyl derivative occurs in the ripe fruits of Pastmaca sativa (Renesse, A 166, 80). Heated with ammoniacal ZnCl, at 280° it yields a mixture of mono- di- and tri- octyl-amines, the yield of

mixed bases amounting to 70 per cent of the alcohol used (Merz a Gasiorowski, B 17,629)

Acetyl derivative C.H., OAc (212° cor)

S.G. § 8847 (G); ½ 8744, ½ 8678 (P) C.E. (0°-10°) 00094. S.V. 2458 (Gartenmeister) M M 10 601 s+ 16 1° (Perkin, C. J 45, 421)

Ethylether C.H., OEz (306°)

Ethylether C.H., OEt (183°) S G 11 79.

Sec Octyl alcohol O.H.; CH(OH) CH.

pryl alcohol Methylber (1940) Capryl alcohol Methyl-hexyl-carbinol (1795° cor) SG $\frac{15}{15}$ 8236, $\frac{25}{15}$ 8178 MM 9 004 at 12 4° (Perkin) SV 191 3 (Schriff, A 220, 103) $\mu_S = 14297$ B_{∞} = 65 57 (Bruhl, A 203, 28) Formed by distilling sodium rianoleate with NaOH (Bours, A 97, 34, Moschinin, A 87, 111, A Ch [3] 44, 140, Limpricht, A 93, 242, Neison, C J 27, 837, Schorlemmer, Pr 16, 376, C J 27, 1029) Obtained also from n-octane via octyl chloride and octyl acetate (Schorlemmer, A 152, 152) Yields methyl hexyl ketone on **ox**idation

(193° Acetyl derivative C.H.,OAc Octyl alcohol C₆H₁₀O Di-isobutyl hydrate (180°) SG ²/₂ 841 Formed by chlorinating CH₂Pr CH₂Pr, converting the resulting octyl chloride into octyl acetate, and boiling this with KOHAq (W C Williams, C J 35, 127) Yields

an octoic acid on oxidation

Octyl alcohol C_sH₁₈O (c 162°) SG 14 820 Formed at the same time as the preceding (W) Yiel C.H. CO C.H. (160°) Yields on oxidation a ketone

Octyl alcohol CHEt, CH(OH) C,H, Formed from CH, Br COBr and ZnEt, followed by water (Winogradoff, A 191, 125)

Sl sol water

Octyl alcohol C.H.,O (174°-178°) SG 2 811 Obtained from octylene, by treatment with HI, the resulting octyl iodide being converted into octyl acetate by AgOAc (De Clermont, C R 66, 1211, A 149, 38, Bl [2] 12, 212) Yields a ketone CaHieO on oxidation, and, on further oxidation, acetic and hexoic acids probably identical with methyl-hexyl-carbinol

Acetyl derivative (c 176°)

Tert Octyl alcohol Pr.CMe(OH) (161 5° cor) 8 G 3 8236, 3 8151 Formed from di propyl ketone, MeI, and zinc, followed by water (Sayt-vaff J mr [2] 31. 320. Bl [2] 45,257) Yields zeff, J pr [2] 81, 820, Bl [2] 45,257) Yields acetic, propionic, and butyric acids on oxidation

Acetyl derivative (c 175°) BG 😵

(160 5°) 8 G 20 838 8554

Tert Octyl alcohol CEt.Pr(OH) Formed from butyryl chloride or EtCOPr and ZnEt, followed by water (Butlerow, Bl [2] 5, 17, Sokoloff, J R 1887, 595) Yields butyric, propionic, and scetic acids on oxidation

Acetyl derivative (177°)

Octyl alcohol CMe, CH, CMe, (OH) Isodibutol. [c - 20°] (147°) SG 2 842 Formed from 'di isobutylene' hydroiodide and Ag.O (Butlerow, A 189, 58). Yields CMe, CO, H and acetone on oxidation

Sec-Octyl alcohol (182°-186°). Obtained from n-octane by chlorination and conversion of the mixed octyl chlorides into acetates (Schorlemmer) Yields propionic and valeric acids on oxidation

Acetyl derivative OCTYL ALLOPHAN. ALLOPHANATE C,H,N,O, C_sH₁,O CO NH CO NH. [156°] Formed from octyl alcohol and Cl CO NH. (Gattermann, A. 244, 40) Silky needles, v. sol hot alcohol

n-OCTYLAMINE C.H., NH. (186°) (E) (180°) (H. a D) Formed, together with di- and tri octyl amine, by heating octyl iodide with alcoholic NH, at 100°, or octyl alcohol with ammoniacal ZnCl₂ at 280° (Renesse, A 166, 85, Merz a Gasiorowski, B 17, 629) Formed also by reducing nitro octane (Eichler, B 12, 1885), and produced by decomposition of the urea C₈H₁₇NH CO NH CO C₈H₁₇ [100°], which is pro duced by the action of KOBr on ennoic amide C₂H₁, CO NH₂ (Hofmann, B 15, 773, Hoogewerff a. van Dorp, R T O 6, 387) Oil.—B'HCl— B'₂H_PtCl₄—Picrate [113] Plates (H a D)

Sec-Octylamine C.H., CH(NH₂) CH., Caprylamine (175°) (B), (163°) (Jahn, M 8, 172). Formed, together with the di- and tri-octylamines, by heating iso outyl chloride with aqueous NH, (Malbot, O R 105, 575, A Ch. [6] 13, 507, cf Squire, C J 7, 108, Cahours, A 92, 399, C R 39, 254, Bouis, A Ch. [8] 44, 139) Formed also by heating the alcohol with ammoniacal ZnCl, at 260° (Merz a. Gasiorowski, B 17, 634)—B'HCl—B'HI— B'HAuCl, -B',H,PtCl, -B'HNO, -B',H,SO,: crystalline, v sol water

D1 n-octyl-amine $(C_8H_{17})_2NH$ [37°] (298°) VD 827 (obs)—B'HCl—B'₂H.PtCl₆ insoluble yellow plates (M a G)

(260°-270°) Di-180-octyl-amine (obs) —B'HCl —B'HAUCl, —B',H,PtCl,

Tri n-octylamine (O,H₁₁),N (367°) Solid,
sl. sol 90 p c alcohol —B',H,PtCl,

Tri -so-octylamine (C,H₁₁),N (0 370°) Oll.

-B'₂H₂PtCl₄ reddish brown mass n-OCTYL-BENZENE C.H., C.H. (263°) SG 15 849 Formed from bromobenzene, *-octyl bromide, and sodium (Schwei-

nitz, B 19, 641, Ahrens, B 19, 2718) Octyl-benzene Pr CH₂(CH₂), C₅H₅ 255°) Formed by heating phenacyl isoamylmalonic acid with zinc-dust (Paal a Th Hoff mann, B. 28, 1502) Oil, with blue fluores-

cence

References -- Bromo, Chloro-, and Iopo-OCTYL-BENZENE and OCTYL-PHENYL AMINE

n-OCTYL-BENZENE SULPHONIC C.H., C.H., SO.H. Formed by sulphonation of n-octyl-benzene (Schweinitz, B 19, 642)— BaA', aq -PbA', 3aq -AgA'aq minute soluble prisms

n-OCTYL-BENZOIC ACID C₁₅H₂₂O₂ Formed by C₂H₁, C₄H₄ CO₂H[1 4] [139°] saponifying its nitrile which is obtained by distilling the formyl derivative of p octyl-phenylamine with zinc-dust (Beran, B 18, 188).
Plates or needles —AgA'

Natrale C.H., C.H. CN (c 812° uncor.).

OCTYL BROMIDES Formed from the corresponding alcohols, Br, and P (Zincke, A. 152, 5, Lachovitch, A 220, 181).

 $CH_{a}(CH_{2})_{a}CH_{2}Br$ (199°) (Z), (204° cor) rkin) SG 15 1 1180, 35 1 1099 C_cH₁₂ CHBr CH₂ (188°) SG 22 1 099 (Perkin)

OCTYL CARBAMATE NH₂ CO₂C₆H₁₇ [55°]. (281°) Formed from sec octyl (capryl) alcohol and ONOl at 100° (Arth, Bl [2] 45, 703, A Ch [6] 8, 430) Crystals, v sol alcohol

n OCTYL CHLORIDE CH3 (CH2) CH2Cl Mol w 1485 (180°) (Zincke, A 152, 4), (11 cor) (Perkin) S G 15 8786, 25 8719 M 10 128 at 18° Formed from n octyl alcohol (183° M M

Sec Octyl chloride C.H., CHCl CH. (172° cor) S G 15 8708, 25 8639 M M 10 248 at 18° (Perkin) Formed from sec octyl alco hol and HCl (Bours, A 92, 398, Malbot, Bl Obtained also, together with the [3] 3, 68) preceding isomeride, by chlorinating n octane

(Schorlemmer, A 152, 152)
Octyl chloride Pr CH₂CH₂CHMe CH₂Cl mixture of this chloride with Pr CH, CHCl Pr is formed by chlorinating PrCH_CH_Pr (Williams, C J 35, 127, cf Schorlemmer, A 144, 190)

Octyl chloride CMe₃ CH₂.CClMe₂ (145°-150°) SG 2 890 Formed from 'dusobutylene' and HCl at 100° (Butlerow, A 189, 51)

Octyl chloride CEt2PrCl (155°) (Butlerow,

Bl 5, 24)

n-OCTYLENE C₈H₁₆ Octene (123°) SG 17 722 Formed from n octyl alcohol, I, and P

(Moslinger, A 185, 52)

Octylene C₈H₁₆ (123°) at 750 mm S G 9 7294 (S), 2 7197 (Bruhl, A 235, 11) C E (9 9-123 4) 00138 μ_D 1 413 S V 177 2 (Schiff, A 220, 90) Formed by heating sec-octyl alcohol with H₂SO₄ or fused ZnCl₂ (Bouis, A 92, 396) Formed also, together with octyl bromide, by the action of P and Bi on sec octyl alcohol (Lachovitch, A 220, 185) It is also a product of the action of NH, Aq on sec octyl iodide at 150° (Malbot, A Ch [6] 13, 514) Oil, with unplea sant odour Not affected by cold alcoholic KOH Is perhaps identical with the preceding octylene

Octylene CMe, CH CMe, Dissolutylene (108° 1 V) (B), (112°) (Malbot, A Ch [6] 19, 370, C R 108, 957) S G 2 734 H C 1,252,500 HF 51,500 Formed by polymerisa on of isobutylene by heating with H₂SO₄ (1 pt) and water (1 pt) at 100° (Butlerow, B 8, 1683, 9, 1687, A 180, 245, 189, 44, J R 1882, 190, Konovaloff, Bl [2] 34, 334) Yields acetone, CMe, CO,H, and oxy octoic acid on oxidation

Octylene CMePr CHEt (120 4° cor) SG 29 7314 Formed in the action of MeI and Zn on

di propyl ketone (Sokoloff, J pr [2] 39, 444) Octylene CEtPr CHMe or CEt, CHEt (119°) SG W 7865 A product of the action of EtI and zine on ethyl propyl ketone (Sokoloff, J pr [2] 39, 440) Oil Yields acetic, propionic, and butyric acids on oxidation

Octylene PrCH CHPr (116°-120°) Formed from PrCH(OH) CH(OH)Pr and HI at 140°. followed by alcoholic potash (Fossek, M 4, 673)

Octylenes of undetermined composition have been prepared by Schorlemmer (A 125, 118), Cahours (J 1850, 402, 1863, 529), Renard (BI [2] 39, 541), Wurtz (A 128, 230), Cloéz (B 7, 823), Williams (B 10, 908), Thorpe a Young (A 165, 14), and Fittig (A 117, 77)
OCTYLENE BROMIDE v DI BROMO OCTANE

OCTYLENE GLYCOL v DI-OXY-OCTANE

OCTYLENE OXIDE C.H., O (145°) S.G. 15 831 Formed by the action of KOH at 180° on the chloro cetyl alcohol formed by union of octylene with HOCl (Clermont, C R 68, 1323)

n-OCTYL IODIDE C.H.,I (220°) (Möslinger, B 9, 998), (225 5°) (Dobriner, A 243, 29) S & § 18533 (D), \$\frac{1}{2}\$ 13407, \$\frac{2}{3}\$ 13316 (Perkin). C E (0°-10°) 00089 (D) MM 16 197 at 20 7° S V 222 6 Formed from the alcohol and HI

Sec-Octyl 10dide C.H., OHMeI (211°) S G 18 1 31 (B), 2 1 355 (Krafft, B 19, 2222) Formed from the alcohol (Bours, A Ch [3] 44,

131, Squire, O J 7, 108)
Octyl iodide C_aH₁, I (120° in vacuo) S G
11 1 314 Formed from octylene and HI (De

Clermont, Bl [2] 12, 212)
DI-OCTYL-MALONIC ACID C₁₉H₃₆O, 1.4 (C₈H₁₇)₂C(CO₂H)₂ [75°] Crystals, nsol water (Conrad a Bischoff, B 18, 597, A 204, 163) Ethyl ether Et₂A" (338°) S G ½ 896 OCTYL NITRITE C₈H₁, O NO (176°) S G

17 862 Formed from octyl alcohol and HNO, (Eichler, B 12, 1887)

Sec Octyl nitrite O.H.; CHMe O NO (165) SG 2 881 Formed by the action of glyceryl trinitrite on sec-octyl alcohol (Bertoni, G 16,

Oll, v sol ether OCTYL OXIDE (C₂H₁₇)₂O (0° 10°) 00088 S V C.H. ON: SG g sÝ \mathbf{CE} 4036 Formed from C,H,ONa and C,H,I (Moslinger, A 185, 56, Dobriner, A 243, 10)

o OCTYL-PHENYL-AMINE C.H., C.H. NH.,

-B'HCl -B'₂H₂SnCl₄ (Ahrens, $\stackrel{.}{B}$ 19, 2725) p Octyl-phenyl-amine [20°] (310° co (310° cor) Formed by heating octyl alcohol with aniline and ZnCl₂ at 280° (Beran, B 18, 132) —B'HCl — B'2H2SO4 -B'2H2C2O4. white plates

Formyl derivative [56°] Plates Acetyl derivative C14H2 NHAc [93°] Benzoyl derivative [117°] Plates The corresponding derivative of sec-octyl phenyl amine melts at 109°

n OCTYL-PHOSPHINE C₈H₁₇PH₂ (c 186°) SG 17 821 Formed by heating octyl rodide with PH,I and ZnO (Möslinger, A 185, 65) -B'HI crystalline

OCTYL SULPHATES

n Octyl-sulphuric acid C₈H₁,O SO₉H (Mös linger, A 185, 62) Forms a sparingly soluble Ba salt, and an easily soluble K salt

Sec Octyl-sulphuric acid C₈H₁₇O SO₈H Bours, C R 33, 144, 38, 935) -BaA'. Saq pearly crystals

n ÔCTYL SULPHIDE (C₈H₁₇)₂S (above 810°) S G 17 842 From the chloride and K₂S (Möslinger, A 185, 59)

Sec OCTYL SULPHOCYANIDE C.H., NS & 6 C.H., CHMe S Cy (142°) From the rodide and potassium sulphocyanide (Jahn, B 8, 805)

OCTYL-THIENYL METHYL KETONE $C_4H_2S(C_8H_{17})$ CO CH, (c 352°) Formed, together with only $C_4HS(C_8H_{17})$ (CO CH₃), (which yields an oxim [58°]), by the action of AcCl on octyl thiophene in presence of AlCl, (Schweinitz, B 19, 646) Oil, volatile with steam

n-OCTYL-THIOCARBIMIDE C₈H₁, N CS (232°) Formed from n-octylamine (Jahn, B 8, 804, M 8, 178)

(a)-OCTYL-THIOPHENE C,H,, C,H,S (258°). SG 205 8118. Formed from octyl bromide, (a) iodo thiophene and Na in ether (Schweinitz, B 19, 644) Oil

References - BROMO- and IODO OCTYL THIO-

OCTYL-THIOPHENE DICARBOXYLIC **ACID** C_8H_1 , $C_1HS(CO_2H)$, $[185^\circ]$ Formed by oxidising $C_1HS(C_8H_{1,1})(CO\ CH_3)_2$ with alkaline KMnO₄ (Schweinitz, B 19, 646) Needles — BaA" $1\frac{1}{2}$ aq — $CuA'' 2\frac{1}{2}$ aq — $Ag_2A'' 3$ aq yellow pp Sec OCTU-THIO-UREA C_8H_1 NH CS NH_2

Formed from sec octyl thio carbimide and NH, (Jahn, B 8, 804, M 3, 173) Plates OCTYL TOLYL AMINE $C_0H_2Me(C_0H_1)NH_2$ Plates

 (325°) Formed by heating o toluidine with octyl alcohol and ZnCl, at 280° (Beran, B 18, $O1 - B'HCl - B'_2H_2SO_4 - B'_2H_2C_3O_4$

Acetyl derivative [81°] Needles Benzoyl derivative [117°] Plates OCTYL UREA Ennoyl derivative C₈H₁,NH CO NH CO C₈H₁, [97°] From ennoice amide, Br, and NaOHAq (Hofmann, B 15, 760)

CENANTH DIACETONAMINE v. ACETON-

AMINE

ENANTHIC ACID v HEPTOIC ACID CENANTHOL v HEPTOIC ALDEHYDE ENANTHYLAMINE v HEPTYLAMINE ENANTHYLIC ACID v HEPTOIC ACID **ENANTHYLIDENE** v HEPTINENE

ENOGLUCIN C,H,O, [208 5°] stance resembling phloroglucin prepared from cenolin, the red colouring matter of wine, by potash fusion (Gautier, Bl [2] 33, 583) Tables (containing 2aq), m sol water Gives no colour with FeCl

CENOLIN C 1H-0O10? A colouring matter ppd by adding lead subacetate to red wine (Glénaid, C R 47, 268, Gautier, Bl [2] 32, 103) or by adding lime (Varenne, Bl [2] 29, 109) Its composition is variable

Delivatives of $\langle_{ m N~CH}^{ m N~CH}\rangle_{ m S}$ **QIAZTHIOLES**

OILS Liquids nearly or quite insol water In a more restricted sense, the term oil is applied to neutral liquids derived from plants or animals Oils are said to be 'fixed' when they cannot be distilled either alone or with steam without under going decomposition, oils that can be so dis-tilled being termed volatile or essential oils Most of the fixed oils are glycerides of sterric, palmitic, and oleic acids (i GLYCERIN) Latty oils that absorb oxygen from the air and thus become slowly converted into varnishes are termed drying oils, e g linseed, hazel nut, hemp, and poppy oils Diying oils contain glycerides of linoleic and similar unsaturated acids (v Lino LEIO ACID and FAT) Essential oils consist either wholly of hydrocarbons or of mixtures of hydrocarbons with compounds of carbon, hydro gen, and oxygen These oxygenated compounds may be compound ethers (oil of chamomile), phenols (oil of thyme, oil of caraway), ketones (oil of rue), aldehydes (oil of cinnamon), or acids Many essential oils deposit a (oil of valerian) solid (stearoptene) on cooling strongly, leaving a liquid portion (elæoptene) Most of the essential oils contain terpenes or at any rate hydrocarbons of the formula (CoHe), (v TERPLNES) The individual oils are described in their alphabetical places See also FAT

OLEANDRINE. A poisonous alkaloid [70°-75°], in the leaves of the cleander (Lukomski, J.

1861, 546, Betelli, J 1875, 783) Minute crystals (by sublimation)

OLEFINES Hydrocarbons, C_nH_{2n}, homologous with ethylene, so called from their property of combining with chlorine and bromine, even in the dark, forming oily dichlorides and dibromides

(v vol 11 p 716) OLEIC ACID C₁₈H₂O₂ Mol w 282 [8°] (Schön, A 244, 262), [14°] (Gottlieb) (223° at 10 mm), (286° at 100 mm) (Krafit a Noerd linger, B 22, 819) S G 12° 808 Occurs as glyceryl ether (triolein, vol 11 p 622) in most fixed oils and fats (Chevreul, Recherches sur les corps gras, p 205, Varrentrapp, A 35, 196, Laurent, A Ch [2] 65, 149, Gottheb, A 57, 40, Heintz, P 83, 555, 89 583, 90, 143, Berthelot, A Ch [3] 41, 243) Prepared by saponifying olive or almond oil with potash, decomposing the soap with taitaric acid, heating the separated fatty acids with PbO, extracting lead oleate with ether, shaking the extract with HClAq, decanting and evaporating the ethereal solution

Propertus -White needles or (above 14°) oil. Insol water, v sol alcohol, miscible with ether May be distilled by superheated steam at 250° Neutral to litmus, but when impure it absorbs oxygen, becoming acid and rancid Gives a cumson colour (Pettenkofer's reaction) when heated with sugar or furfuraldehyde and H.SO.

(Mylius, H 11, 492)

Reactions -1 Yields, on distillation, sebacic, acetic, and hexoic acids, CO_{2} CH₄, C_{2} H₄, and CO (Engler, B 22, 593) -2 Potash fusion gives acetate, palmitate, and hydrogen -3 Nitrous acud converts it into the isomeric elaidic acid, which is solid -4 Nitric acid oxidises it to acetic, propionic, butyric, valeric, hexoic, heptoic, octoic, ennoic, decoic, suberic, pimelic, adipic and azelaic acids -5 Glycerin yields on heating mono and tri olein -6 Bromine combines, forming di-bromo stearic acid (Overbeck, J pr 97, 159) -7 HIAq and red P at 205° in sealed tubes yield stearic acid (Goldschmiedt, Sitz W 72, 366, Muter, An 2, 63) —8 Alkaline KMnO gives azelaic acid and di oxy stearic acids [137°] (A Savtzeff, J pr [2] 31, 541, Bl [2] 45, 255) 9 Iodine (1 p c) in sealed tubes at 270° forms steam and (Wilde a Reychler, Bl [3] 1, 295) 10 Cone H.SO., followed by water, yields oxysteam and (79°), oxy steam actions [48°], and other (H.C.) of the cone (18°), and other (H.C.) of the cone (18°). orly C₁₆H₃₃ CH(O SO₃H) CO₂H (Sabanéeff, Bl [2] 46, 819, Geitel, J pr [2] 37, 74) Salts — KA' S 25 in the cold

Deliquescent Its solution deposits a gelatinous acid salt when greatly diluted —NaA' S 10 at 12° S (alcohol of S G 82) 5 at 13° S (bollong ether) 1 - Jah' Cold S (boiling ether) 1 – LiA' — CaA'₂ granular pp — SrA'₂ — BaA'₂ crystalline — BaH.A'₄ flocculent (Gossmann, A 86, 322) — MgA'₂ — PbA'₂ [c 80°]. White powder, sol boiling ether, turpentine oil and ligroin -Pb,A' O [100°] -Pb,A',O, (Schon). -MnA sl sol alcohol, v sol ether -FeA'2 insol alcohol, v sol ether -- AlA'3 sl sol ether -Hg A'₂ grey flocks, insol water, sol alcohol and ether -ZnA'₂ -CuA'₂ -AgA' Methyl ether MeA' S G ¹² 88 Oil

(307°) at 307 mm MM 219 at 15° Ethyl ether EtA' $875, \frac{95}{25}$ 870 S G (Perkin)

Glyceryl derivatives v vol 11 p 622 Amids C,H,O(NH,). [78°] (R), [75°] (C) Formed by the action of alcoholic ammonia on oil of almonds or oil of hazel-nuts
(Rowney Cl. 7, 200, Coolet P. 1950, 72)

(Rowney, C. J 7, 200, Carlet, Bl 1859, 78).

Eladic seid. [47°] A polymeride of cleic acid produced by the action of nitrous acid on cleic acid. It may also be got by saponifying its glyceryl derivative, elaidin, which is formed when clive oil is solidified by nitrous acid gas or by mercurous nitrate (Boudet, A Ch. [2] 50, 391, Laurent, A Ch. [2] 65, 149, Meyer, A 85, 174, Gottlieb, A 57, 54) Laminæ (from alcohol), m sol ether May be distilled Acid to litmus. On fusion with potsash it yields acetate and palmitate Alkaline KMnO, forms di-oxy stearia acid Combines with bromine forming di-bromo-stearic acid [27°] (Burg, Bl [2] 3, 191).

Salts—NaA' plates—NaHA'.—AgA' Methyl ether MeA'. S G 18 872 Oil Ethyl ether EtA' S G 18 869

Glyceryl ether C.H.A'. Flaidin [82°] Nodules, almost insol alcohol.

Amide [94°] Formed from elaidin and alcoholic NH, Needles

Iso-oleic acid $C_{18}H_{14}O_{2}$ [45°] Formed by the action of alcoholic potash at 120° on iodostearic acid obtained from oleic acid and HI (Michael a. Saytzeff, J pr [2] 35, 886, 37, 277, Benedikt, M 9, 520). Got also by distilling, at 100 mm pressure, oxy-stearic acid (v OLEIO ACID, Reaction 10) Trimetric plates (from ether), insol water, v e sol. alcohol, m sol ether

Reactions—1 Yields acetate and palmitate by potash fusion.—2 KMnO₄ forms di-oxysteance acid [78°]—8 Bromme forms a liquid dibromide—4 HI yields an oily iodosteance acid.

Salts -NaA' -ZnA'.

OLEIN v GLYCERIN, Oleyl derivative.

OLIBANUM Incense A gum resin exuding from Boswella papyrnjera. It contains 7 p c essential oil, 72 p c of resin soluble in alcohol, and 20 p c of gum (arabin) (Stenhouse, A. 35, 306, Kurbatoff, Z [2] 7, 201, A 173, 1, cf Braconnot, A Ch [2] 58, 66) The essential oil contains a terpene, olibene CloHie (157°), S G 12 863, and an oxidised substance Olibene forms a hydrochloride CloHie Hcl [127°]

OLIVE OIL SG 40 918 (Long, Am 10, 892) An oil expressed from olives (Olea europæa) It contains the glyceryl ethers of oleic and palmitic acids. The glycerides of unsaturated acids are present in greater quantity (87 pc) than those of saturated fatty acids (18 pc) (Hazura a Grüssner, M 10, 248)

olivil $C_{14}H_{18}O_{5}$ [120°] A neutral substance occurring, together with resin and a little benzoic acid, in the gum of the olive tree. The Tresin is removed by ether, and the residue crystallised from alcohol (Pelletier, A Ch [2] 3, 105, 51, 196, Sobrero, A 54, 67, Amato, G 8, 83) Anhydrous crystals (from alcohol) or prisms containing A (from water) Reduces silver salts. Alkaline KMnO4 yields vanillin Conc HIA4 yields MeI and EiI.

OMICHOLIN C_{2,}H₃₀NO₅? A red resin obtained, together with the similar omicholic acid from urine (Thudichum, C R 106, 1803)

OMPHALOCARPIN A neutral substance in the fruit of *Omphalocarpum Procera* (Naylor, Ph [3] 12, 478) Needles (from alcohol) ONOCERIN $C_{12}H_{10}O$. Occurs, together with ononin, in the root of *Ononis spinosa* (Hlasiwetz, J. pr. 65, 142). Hair-like crystals (from alcohol) Ohlorine forms resinous $C_{12}H_{10}Cl_2O$.

ONONIN C₂H₂O₁₂ [235°] Aglucoside occurring in the root of the spinous rest-harrow (Ononis spinosa) (Reinsch, Rep Pharm [2] 26, 12, Hlasiwetz, Stts W 15, 142) Tasteless needles (from alcohol), sl. sol boiling water, nearly insol ether Its alcoholic solution is ppd by lead subacetate

Reactions —1 Boiling baryta-water splits it up into formic and and crystalline oncospin $C_{22}H_{24}O_{12}$ [162°] —2 Dilute $H_{25}O_{4}$ yields glucose and formonetin $C_{24}H_{25}O_{5}$, which is further split up by baryta-water into formic acid and oncoetin $C_{25}H_{25}O_{5}$ [120°] Formonetin and oncoetin crystallise from alcohol Oncoetin and oncospin are coloured red by FeCl₂

OPHIOXYLIN O, H, O, ? [72] S 15 at 100°, S (alcohol) 33 at 78° Occurs in the root of Ophioxylon serpentinum (Bettink, R T C 8, 319) Dimetric needles Conc H, SO, colours it blood-red and, on warming, indigo blue Its alkaline solution is violet

OPIANIC ACID C₁₀H₁₀O₃ i.e.

C_sH₂(OMe)₂(CHO) CO₂H Mol w. 210. [146°]

An acid obtained by the exidation of narcotine

(q v) (Liebig a Wöhler, A 44, 126, 50, 1,

Blyth, A 50, 29, Anderson, Tr E 20 [2] 347,

Matthessen a. Foster, C J 16, 345, 21, 357)

It is also formed by the action of KMnO, and
dilute HNO₂ on hydrastin (Freund a Will, B 19,
2799) Purified by passing a rapid current of
nitrous acid gas (which does not affect it)
through its boiling aqueous solution (Frinz, J pr

[2] 24, 355) It may also be purified by ether
fication, the ether being subsequently decom
posed by boiling with water (Liebermann a
Kleemann, B 20, 881)

Properties — Needles or prisms, v sol alco hol, ether, and hot water Tastes bitter

Reactions -1 Readily oxidised to hemipic acid -2 Reduced by sodium-amalgam to meconin — 8 Boiling cone KOHAq yields hemipic acid and meconin — 4 Cone HClAq at 100° yields MeCl and C,H,(OMe)(OH)(CHO)CO,H. HIAq acts in like manner Dlute HClAq at 170° forms isovanillin C_sH_s(OMe)(OH)CHO and protocatechuic aldehyde —5 HNO, forms nitroopianic acid, nitro-hemipic acid, and a compound C₂₀H₂₀N₂O₁₂.—6 PCl₂ yields a chloride reduced by zinc and HCl to meconin —7 Heating with malonic acid, HOAc, and NaOAc forms $C_sH_s(OMe)_s$ $C_cH_s(OH_s, CO_sH)$ $C_sH_s(OMe)_s$ C_sH_s 19, 2284) -8 H.SO. (30 pts') at 180° forms rufiopin, a red colouring matter (Anderson, C J 9, 277, Liebermanna Chojnacki, B 4,194) - 9 Dis tillation with soda-lime yields methyl-vanillin. 10 Tolylene-o-diamine forms a crystalline com-To Victor-auditivite torins a crystalline compound [248°] (Bistrzycki, B 21, 2528) —11 Benstaine yields O₂₄H₂₄N₂O₈ [above 320°] —12 Urea forms C₁₁H₁₂N₂O₈ [259°] —18 Hydrasobensens produces C H₂(OMe)₃ CH(NPh NHPh) [188°] 14 An alcoholic solution of hydroxylamine hydrochloride forms, on boiling, hemipimide, but

in the cold it yields the isomeric oxim-anhydride C_sH₂(OMe)₂CO O [115°] (Liebermani, B 18,

OPIUM. 639

2928). This body suddenly changes, at its melting point, to hemipimide, with great rise of temperature.—15 Antime in HOAc forms, on boiling, C.Hi(OMe),(CO.H)CH NPh [1879].—16 Ammynea forms opiammon C₂₀H₁₁NO₈, a yellowish powder, decomposed by water at 150° into NH₂ and opianic acid.—17 Aqueous sulphurous acid forms crystalline C₁₀H₁₀O₃H₂SO₃, whence the salts BaA'₂ Saq and PbA'₂ baq may be obtained.—

18 H₂S forms yellow amorphous C₁₀H₁₀SO₄—

10 D₁C₂C₃A'₂SO₃ SO₃ Aboli (1900) 19 Phenol and H2SO, in the cold form amorphous opnaum C₂₀H₁₀O₂, which forms a purple solution with potash — 20 Phenyl hydrazine acetate forms C₁₆H₁₆N₂O₃ crystallising in needles [175°] (Lieber mann, B 19, 763) — 21 Salicylic acid and ZnCl₂ form C₁₆H₁₀O₃ [140°], whence C₁₆H₂AcO₃ [152°] (Michael, Am 5, 95)

Salts -KA'2 aq (Wegscheider, M 8, 348) -KA'aq triclinic plates -BaA', 2aq efflorescent prisms -PbA', 2aq sparingly soluble crystals [150°] -PbA', tufts of silky prisms -AgA'

Methyl ether MeA' [85°] (W), [102°] (L) Formed from the silver salt and MeI, or by boiling the acid with MeOH. Monochinic

Propylether PrA' [10] [103°]

acu, [121°] [111°] Na Acetyl derivative CieH.AcO, Propionyl derivative

Needles Anhydride {C₆H₂(OMe)₂(CHO) CO}₂O Triopianide [234°] Formed by heating the acid for two hours in a current of dry air Needles (from acetone)

Oxim C₆H₂(OMe) (CO₂H) CH NOH Formed from the acid (1 mol), dilute KOH (4 mols), and hydroxylamine hydrochloride (1½ mols) in the cold (Perkin, jun, C J 57, 1071) Long slender needles, v sol alcohol At 130° it suddenly becomes solid owing to the formation of hemipimide

Di phenyl-hydrazide

C₆H₂(OMe)₂(CO₂H) CH N NPh₂ [172°] Ca A' 8aq

Chloro-opianic acid C,HCl(OMe) (CHO) CO,H

[211°] Needles (Prinz, J pr [2] 24, 366)

[192°] (P), [204] Bromo-opianio acid Needles -BaA', aq (Wegscheider, M 4, 267)

Nitro-opianic acid C_bH(NO₂)(OMe)₂(CHO) CO₂H [166°] Formed by nitration of opianic acid (Prinz) Yellow prisms (from water) With acetone and dilute NaOHAq it yields the tetra-methyl derivative of tetra oxy indigo dicarboxylic acid (Liebermann, B 19, 352) Aniline in HOAc reacts, forming C₄H(NO₂)(OMe)₂(CO₂H) CH NPh [184°] — KA' 3aq prisms —BaA'₂ 3aq yellow needles.

[96°] Ethylether EtA'

Acetyl derivative C10H2AcNO, Orystals

Phenyl-hydrassde

C₆H(OMe)₂(NO₂)(CO₂H) CH N₂HPh [184°] Red needles (Liebermann, B 19, 764) By boiling with HOAc it is converted into 'nitro-opianylphenyl-hydrazine' O₁₈H₁₂N₂O₅ [178°]

Di-phonyl-hydraside C2H, N.O. [2179] Prisms, sl. sol ether (Bistrzycki, B 21, 2520)

Nitroso-opianic acid? C₂H(OMe)₂(NO)(CHO) CO₂H [6 5 8 4 1] [176° Formed by reducing nitro opianic acid with NaOMe (Kleemann, B 20, 875) Long yellowishgreen needles.-AgA', felted needles.

Amido-opianic acid C₆H(NH₂)(OMe)₂(CHO) CO₂H. Formed by reduction of nitroso-opianic acid (K.). -HA'HCl.

Acetyl derivative O24H24N2O11. [233°]. Phenyl-hydrazide

C.H(NH.)(OMe)2 CO NPh. [143°]. Needles

(Liebermann, B 19, 2276)

Noropianic acid C.H.2(OH)2(OHO)CO2H [1710 Formed by heating opianic acid with

Crystals (containing 1 aq)

Methyl derivative C.H.(OMe)(OH)(CHO) CO.H [154°](P), [142°] (Wegscheider, M 8, 790) Formed by heating opianic acid with HClAq at 100° Prisms (containing xaq) Chlorine forms the chloro-derivative C₂H,ClO₅ [206°] On intration it yields C₂H(NO₂)(OMe)(OH)(CHO) CO₂H [208°], which crystallises in needles (containing aq), and yields an oxim decomposing at 252°, and converted by HOAc into the anhydride C.H.N.O. [252°], the nitro- acid also yields a phenyl-hydrazide [179°] converted by HOAc into an anhydride [191°] (Elbel, B 19, 2306) —KA'2aq —BaC,H,O, aq

Iso opianic acid v Methylderivative of ALDE-

HYDO VANILLIC ACID

Iso-noropianic acid C₆H₂(OH)₂(CHO) CO₂H [4 3 5 1] [above 240°] Formed by heating aldehydo vanillic acid with HClAq at 175° (Tiemann a Mendelsohn, B 10, 400) Needles

Pseudopianic acid C_cH₂(OMe)₂(CHO)CO_cH [1 2 3 4] [122°] A product of the action of boiling dilute H₂SO₄ on berberol (Perkin, jun., C. J., 57, 1065) Slender needles (from hot water) When warmed with phenol and H2SO, it gives a green colour, chan-

oran C₁₀H₁₀O₄(NOH) [124°] Needles

Oxim C₁₀H₁₀O₄(NOH) [124°] Needles

OPIANYL ACETIC ACID C₁₂H₁₄O, te

C₂H₄(OMe)₂(C₃H) CH(OH) CH₂CO₂H Formed as barium salt, by boiling meconin-acetic acid (p 198) with baryta water (Liebermann a Kleemann, B 19, 2292) The acid when liberated from its salts at once loses H₂O and is reconverted into its lactone meconin acetic acid.—
A'Ag crystalline pp —A'₂BaAq prisms

OPINIC ACID C, H,O, [148° Formed by the action of HI on hemipic acid (Liechti, Z [2] 6, 196, A Suppl 7, 151, Beckett a. Wright, J 1876, 809) Prisms (containing 2aq) Coloured

violet by FeCl,

[227°] A substance present in OPIONIN small quantity in Smyrna opium (Hesse, A 228, 299) Small needles, v sol alcohol, ether, and alkalıs, v sl sol water Neutral to litmus When fused with potash it yields opionic acid

OPIUM The dried juice obtained from the unripe capsules of Papaver somniferum It con tains morphine, codeine, narcotine, narceine, thebaine, papaverine, meconic acid, and me-The quantity of morphine varies from 8 to 15 pc Hesse (A 153, 47, Suppl 8, 299) obtained also codamine, lanthopine, laudanine, meconidine, cryptopine, protopine, laudanosine, and hydrocotarnine Kauder describes tritopine (Ar Ph 228, 419) The three alkaloids morphine, codeine, and thebaine are strong bases, while papaverine, narcotine, and narceine are feeble bases The various constituents of opium are described in their alphabetical position

OPOPANAX The dried juice obtained from | the roots of the Pastinaca Opopanax It contains 33 pc of gum, 28 pc of malic acid, and 42 pc of a resin which yields protocatechuic acid on fusion with potash (Pelletier, Hlasiwetz Barth, J 1866, 630, Hirschsohn, C C. 1877,

ORANGE PEEL OIL SG 28 8435 essential oil of orange peel consists mainly of a terpens (174°), but contains also an aldehyde $C_{10}H_{10}O$ (224°-228°) (Wright, C J 18, 1186, 20, 552, Semmler, B 24, 202) It contains no cymene (Hartley, C J 37, 677) Tanret (Bl [2] 46, 501) got from orange peel resinous aurantiamarie acid ' $C_{10}H_{12}O_4$, $[a]_D = -28^\circ$, and incrystallisable 'aurantiamarine' $C_{22}H_{26}O_{12}$? uncrystallisable 'aurantiamarine' $[\alpha]_D = -60^\circ$, a very bitter substance ORCEIN $C_{23}H_{24}N_2O_7$ A colou

A colouring matter obtained from orcin by the action of aqueous ammonia and air Purified by exhausting with ether, and crystallising from dilute alcohol (Zulkowsky a Peters, M 11, 227, cf Robiquet, A Ch [2] 42, 245, 58, 320, Dumas, A 27, 145, Laurent a Gerhardt, A Ch [3] 24, 315, Liebermann, B 7, 247, 8, 1649) Micro crystalline mass, with metallic lustre, insol water, ether, and CS. Its solutions are crimson, but are turned bluish violet by ammonia or potash

ORCENE DIALDEHYDE This name is given by Tiemann and Helkenberg (B 12, 1003) to two isomerides C₆HMe(OH)₂(CHO)₂ (a) [118°] and (B) [168°] formed, together with oroyl aldehyde C,H₂O₃, by the action of chloroform and KOH upon orein The (a)-isomeride forms a di anilide C,HMe(OH),(CH NPh), [281°]

ORCIN C,H₂O₂ & c C,H₃Me(OH) [1 3 5] D₂-

Methyl resorcin Mol [108°] (Nevile a Winther, C J 41, 417), [57°] (when containing aq) (c 288) H F p 109,276 (Stohmann, J pr [2] 34, 315) Obtained by boiling orsellic acid with water or by action of alkalis on lecanoric, erythric, and evernic acids and picroerythrin, and also by dry distillation of the same bodies (Robiquet, A Ch [2] 42, 245, 58, 820, Liebig a Will, A 27, 147, Dumas, A 27, 140, Schunck, A 41, 159, 54, 269, Stenhouse, Tr 1848, 85, A 68, 93, 99, Pr 12, 263, C J 16, 327, 20, 223, De Luynes, A 128, 330, 130, 81, Lamparter, A 134, 256) Formed also by potash fusion from aloes (Hlasiwetz a Barth, A 134, 287), p-chloro toluene sulphonic acid (Vogt • Henniger, C R 74, 1107), toluene m disulphonicacid, s-bromo cresol, s di bromo toluene, and s brome toluene sulphonic acid (Nevile a Winther, C J 41, 417) Formed also from nitrom cresol by reduction and application of the diazo reaction

Synthesis — Acetone - di - carboxylic ether $OC(CH_2 CO_2Et)_2$ when treated with sodium condenses to di-oxy phenyl acetic di carboxylicether C₆H(OH)₂(CO₂Et)₂ CH₂ CO₂Et, the latter by the energetic action of alkalis is converted into dioxy phenyl-acetic acid C₈H₃(OH)₂ CH₂ CO₂H, whose silver salt on dry distillation yields orcinol (Cornelius a Pechmann, B 19, 1446)

Properties - Monoclinic prisms (containing aq), v sol water, alcohol, and ether Sweet taste Turns red in air Its aqueous solution gives a white pp with lead subacetate and a dark red pp with FeCl. It reduces ammoniacal AgNO Dry bromine forms tri bromo-ordin

Bromine water yields penta-bromo-orein (Stenhouse a Groves, $C\ J$ 37, 4C3) Its solution is not rendered acid by borax. Nitrous acid gives an orange pink colour in dilute solution. (Linde, C N 58, 1, 15) It forms a deliquescent cora-

pound with pieric acid

Reactions -1 Air and ammonia yield orcein together with yellow Col H10NO, soluble in ether and an amorphous body, resembling litmus, in soluble in ether and alcohol (Zulkowsky a Peters, M 11, 227) Dry ammonia forms colour less crystals of C,H,O,NH, -2 Ammonium carbonate yields 'para orsellic' acid CsH,O, aq [151°] (Senhofer a Brunner, C J 40, 265)—3 KOH and CO, form pseudo orsellic acid (Schwarz, B 13, 1643)—4 Heating with HOAc (13 pts) and ZnCl₂ (2 pts) forms crystalline $C_{27}H_{24}O_2$ as well as 'orcacetein' $C_{18}H_{18}O_4$, a yellow powder (Rasınski, J pr [2] 26, 56) On boiling orcin (9g) with HOAc (135g) and phosphorus oxychloride (18 g) there is formed C₆H Me(OH), CO CH₃ [146°] crystallising in needles -5 Orcin (3 pts) heated with aceto acetic ether (2 pts) and a little H₂SO₄ at 100° forms insoluble C₁₇H₁₆O₅ [249°] which yields C₁₇H₁₅AcO₅ [200°] and C₁₇H₁₅Br₃O₅ crystallising in plates -6 HNO3 saturated with HNO. acting upon an ethereal solution of orcin forms a scarlet dye 'azo orcın ' $C_{14}H_{11}NO_3$ which forms an alkaline solution with orange red fluorescence (Kramer, B 17, 1882) -7 H.SO, saturated with nitrous acid forms a dye C, H, NO, which yields alkaline solutions with red fluorescence and C₂₁H₂₁NO, which does not yield fluorescent solutions (K, Brunner, B 21, 251)—8 A mixture of HNO, and HBr yields C, H, BrNO, and C48H27Me8BrN2O13, the alkaline solutions of these bodies exhibit brown and red fluorescence respectively (Brunner, B 21, 2484) -9 A mix ture of HNO₃ (10 cc of SG 139) and HCl (30 cc of SG 12) on the water bath yields C₁₁H₀ClNO₆, a greenish mass which yields C₁₁H₁₆Ac₄ClNO₆—10 Chloral hydrate and water on boiling form crystalline $C_2H_1O_3$ whence $C_2H_1\circ Ac_3O_3$ [185°] (Michael a Ryder, Am 9, 135)—11 Fusion with NaOH yields resorcin, tetra oxy di phenyl methane, and finally phloro glucin (Barth, M 3, 645) -12 Benzoic aldehyde and a little HClAq give a white resin C22H21O1 (M a R) -18 Chloroform and dilute potash form, on boiling, two isomeric 'orcene dialdehydes 'C, HMe(OH)2(CHO)2 and 'orcyl aldehyde' C.H.Me(OH),CHO [177°] (Tremann, B 12, 999) Another product of the action of potash and chloroform on orcin is homofluorescein (vol ii p 558) which is probably orcin aurin C₂₂H₁₈O₃, a body which is formed by heating ordin with formic acid and ZnCl₂ at 100° (Nencki, J pr [2] 25, 277, Grimaux, Bl [3] 3, 850) -14 Phthalic anhydride (3 pts) heated with orcin (5 pts) and sulphuric acid (5 pts) yields 'or- $-\mathbf{\hat{C}_0H_2Me}(OH)$

cm-phthalein' CeH. COO CeH.Me(OH) which crystallises from acetone in colourless needles, dissolving in alkalis with red colour, and yielding the acetyl derivatives C₂₂H₁₅AcO₅ [150°] and $O_{22}H_{14}Ac_2O_5$ [220°] Orem phthalein is reduced by zine dust and NaOHAq to orem phthalin $C_{22}H_{20}O_5$ which yields $C_{22}H_{18}Ac_2O_5$ [211°] (E Fischer, A 183, 72).—15 Concentrated sulphurie OSMIUM. 641

acid at 70° produces orein disulphonic acid C_sHMe(OH),(SO_sH), which yields the crystalline salts Pb₂O,H,S₂O_s 6gaq and Pb₂(O,H,S₂O_s) 8aq (Hesse, if 117, 324)—16 Fuming HNO, acting of orein dissolved in ether forms prografin C14A11NO2 orystallising in needles [225°] which are blue by reflected light and form a crimson solution in alkalis exhibiting yellow fluorescence Orcirufin yields an acetyl derivative [204°] and an ethyl ether [269°] (Nietzki a Maeckler, B 23, 720) -17 Aldehyde dissolved in alcohol forms on addition of a few drops of HClAq, a compound C₁₈H₂₀O₄ crystallising in tables (Michaela Comey, Am 5, 349)—18 Chloro-acetic acid and caustic soda forms C_sH₂Me(OCH₂ CO₂H)₂ [217°] orystallising in needles This acid forms the salts lising in needles. This acid forms the salts Na.A" 8aq, $K_2A'' 8aq$, and CaA'' 2aq, the ether $Et_2A'' [107^\circ]$, and two intro-derivatives one of which melts at 140° (Saarbach, J pr [2] 21, 162) -19 Di chloro quinonimide in alcoholic solution forms brown needles of 'orcirufamine' C₁₃H₁₀N₂O₂, which dissolves in acids with red dish violet colour and orange fluorescence dyes silk, and yields a crystalline mono acetyl derivative (N a M)

Acetyl derivative C.H.Me(OAc), [25°] Needles, nearly insol water

C.H.Me(OBz). Benzoyl derivative

[88°] Needles (Rasınskı, J pr [2] 26, 65)

Orthocarbonyl derivative [195°] Formed by distilling $(C_6H_3MeO_2)_2C$ C₆H₃Me(O CO₂Et)₂, which is produced by the action of ClCO2Et on sodium orein (Wallach, A 226, 86, Bender, B 18, 700)

 $C_8H_3Me(OMe)(OH)$ Methylether Liquid, sl sol water (Tiemann a (c 278°)

Streng, B 14, 2001)

Di methyl ether C.H.Me(OMe). (244°)

 $\nabla D 762 (H=1) (obs)$ Mobile liquid

Dr ethyl ether C_tH₃Me(OEt)₂ [165°]

2° cor) Needles Yields C_tHBr,Me(OEt)₂ (252° cor) Needles [144°] (Herzig a Zeisel, M 11, 315, cf De Luynes a Lionet, C R 65, 213)

Natroso- derivative C,H,(NO)Or [157°] Yellow needles, detonating at its melting point

(Nietzki a Maeckler, B 23, 723)

References - TRI AMIDO-, AMIDO DI IMIDO-, DI BROMO NITRO, TRI CHLORO, and IODO-ORCIN m Orcin, Iso-orsin, Cresorein, and Luterein DI OXY TOLUENE

B orcin v Betorein

ORCYL ALDEHYDE v DI OXY-TOLDIC ALDE

OREOSELIN C14H12O4 Oreoselone [170°] Formed by the action of alcoholic potash or acids on peucedanin (Wagner, J pr 62, 275, Hlasiwetz, A 174, 70, Heut, A 176, 73) Needles (from alcohol), v sl sol water Its solution in H2SO, exhibits bluish-green fluores-Potash fusion yields resorcin and acetic It yields an acetyl derivative [123°] and an isovaleryl derivative [97°]

[190°] OREOSELONE C₁₄H₁₆O₂ [190°] Formed by passing HCl over dry athamantin (Schnedermann a Winckler, A 51, 820) Needles (from alcohol), insol water

ORGANIC ANALYSIS v. Analysis, obganic, vol 1 p 259

ORNITHINE C.H., N.O. Obtained, together with benzoic acid, by boiling ornithuric acid Vol III

with hydrochloric acid (Jaffé, B 10, 1925) -B',H,Cl, -B'HCl -B',2H,C,O, -B'HNO, Bensoyl derivative C,H,1,BzN,O, [225°-

ORNITHURIC ACID C1. H2. N2O4 Excreted by birds after a dose of benzoic acid-(Jaffé, B 10, 1925, 11, 406) Needles, v sl sol hot water — CaA'2 — BaA'2 powder, v e. sol water

ORSEILLE v ARCHIL

ORSELLIC ACID v DI ONY TOLUIC ACID and LECANORIC ACID

OSAZONES v Hydrazones

OSMATES v OSMIUM, Salts of oxyacids of.

OSMIAMIC ACID v OSMIUM, Nitrogen con taining acid of, p 644

OSMIRIDIUM v IRIDIUM, Alloys of, p 47 OSMIUM OS At w 1903 Mol w un-Infusible at highest temperature at tained by O H flame SG 22 477 at 17 5° (De ville a Debray, P M [4] 50, 651) SH 19° to 98° 03113 (Regnault, P M [4] 23, 103) CE 00000657 (Fizeau, C R 68, 1125)

Occurrence -As metal, alloyed with Ir, Pt. Rh, Ru, and Pd The residues obtained by heating various Pt ores with aqua regia contain from 17 to 50 pc Os (v Deville a Debray, A Ch [3] 56, 431, Berzelius, P 13, 435, 527, 15, 208) In 1804 Tennant showed that the metallic residue remaining after treating Pt ore with aqua regia contained two new metals (T 1804 411), to one of these metals he gave the name iridium, because of the colours of its oxides (fpis = rainbow), and to the other, the name osmium, because of the peculiar smell of its volatile oxide $(\partial \sigma \mu \eta = \text{smell})$

Formation — i By ppg K₂OsO, Aq by NH₄Cl, and heating the pp in H=2 By heating $(NH_4)_2OsCl_3$ or $(NH_4)_2OsCl_3=3$ By strongly heating any of the sulphides of Os in absence of air -4 By warming K perosinate in HClAq, with a formate, or by digesting the same salt with Hg, and heating the Os Hg amalgam thus obtained -5 By passing vapour of OsO, mixed with H or CO through a red hot tube -6 By passing OsO, vapour along with N through a hot tube lined with C (obtained by previously pass

ing C.H. vapour through the tube)

Preparation - When Pt ores are treated with aqua regia, osm iridium remains, partly as lustrous tablets, and partly as a black powder Sand and gangue are removed by fusing the osm-iridium with Na₂CO₃, boiling with water, then with HClAq, and again with water obtained from this residue by various methods, which are based on the ready oxidation of Os to OsO, and the volatility of this compound lustrous tablets of osm iridium yield much more Os than the black powder OsO, may be obtained by the following methods.—1 The osm iridium is heated to redness in a tube of porcelain, or Pt, while a current of air or O (pre-viously passed through H₂SO₂) is sucked through the tube, the exit end of the tube is connected with a dry flask, or a series of dry Woulf's bottles, kept at a low temperature, the connect ing tubes must be wide, else they may get choked with crystals of OsO₄, a vessel containing KOHAq is placed between the receiver and the aspirator, to absorb the last traces of OsO. 642 OSMIUM.

(Fremy, J pr 63, 842) —2 The osm-iridium is very well mixed with an equal weight of dry NaCl, and the mixture is heated to low redness in a rapid stream of moist Cl, in a glass or porcelain tube, the apparatus is connected with a wide necked tubulated receiver, from which a tube passes into KOHAq or NH,Aq OsCl, 18 formed, and decomposed by the H2O present to OsO4, HCl, and Os which again combines with Cl to form OsCl, which OsCl, is again decomposed by H₂O, and so on (Wohler, P 31, 161, 104, 368, 107, 357) Schneider (A Suppl 5, 261) places the osm iridium in a large Hessian crucible, the lid of which is cemented on by CaSO, and carries a porcelain tube passing into a receiver -3 The osm-iridium may be treated with molten KOH and KClO, (Fritzsche, J pr 37, 483), or with KOH and KNO, (Claus, C C. 1862 129, Gibbs, A 120, 108), or with BaO₂ and Ba(NO₃)₂ (Deville a Debray, A Ch [3] 56, 431), in each case the K perosmate obtained is distilled with aqua regia and OsO, is obtained The preparation of OsO, from osm iridium is easily accomplished, but the process is extremely unpleasant, and also very dangerous, masmuch as the vapour of OsO, rapidly attacks the eyes and lungs

Os is obtained from OsO, by reducing the vapour by H or CO, or by C (Deville a Debray, lc, of Formation, Nos 5 and 6), or a solution of OsO, in KOHAQ may be reduced by warming with alcohol, the violet red crystalline pp of K₂OsO, may be dissolved in water, ppd by NH₂Cl, and the pp reduced to Os by heating in H (Fremy, lc) Or the OsO, may be dissolved in NH₃Aq, warmed for some hours till blackish brown (N is evolved, and an ammoniacal solution of Os₂O₃ remains), and evaporated until a brown pp of impure Os₂O₃ forms, the pp may then be washed, dissolved in HClAq, NH₄Cl added, the solution evaporated to dryness, and the residue heated in a retort as long as HCl is evolved and NH₄Cl sublimes Os remains as

a compact porous mass (Berzelius)

Os may be obtained in crystals by dissolving the metal in Sn, by heating to redness in a carbon crucible with 8 parts Sn, and allowing the mass to cool (Deville a Debray, C R 82, 1076) The crystals are purified by dissolving out Sn, and heating the residue in a stream of HCl Os is also obtained in crystals by passing the vapour of OsO₄, mixed with N, through a hot porcelain tube lined with C. The lining of C is obtained by passing C_8H_6 vapour through the tube at a temperature high enough to decompose the C_6H_6 . By alloying Os with Zn, and treating the alloy with HClAq, Os is obtained as a black powder which is easily ignited (D a D, A Ch [8] 56, 899)

Properties and Reactions—As obtained by reducing its compounds at high temperatures, Os is a lustrous, blue-white metal, resembling Pt or Sin Prepared by reduction at lower temperatures, Os is a greyish-black powder, without metallic lustre From solution in Sin, Os separates in hard, bluish crystals, probably belonging to the regular system, Signature at which Rh melts (c 2000°) without fusing it. The Os was placed in a carbon-crucible placed in a cylinder of lime, resting on a block of

lime, and surrounded by three other similar blocks, a powerful O H frame was caused to play over, and around, the lime cylinder (A Ch [8] 56, 385, 61, 5)

Os is easily oxidised to OsO. The findly divided metal obtained at low temperatures smells of OsO4 at the ordinary temperature, when heated in air, it burns and is completely A compact mass of Os ignites when strongly heated in air, but ceases to burn when the source of heat is removed. Os prepared at very high temperatures may be heated to c 225° without change Finely divided Os, which has not been strongly heated, is oxidised to OsO, by heating with conc HNO, or aqua regia, if the metal has been exposed to a very high temperature, it cannot be oxidised in the wet way Os is oxidised, to K2OsO4, by molten KOH, the oxidation is hastened by addition of KNO, or KClO, Heated in Cl, OsCl, is pro duced Os forms a phosphide when heated in P vapour The spectrum of Os has been examined by Huggins (T 154, 139), and Thalén (v B A 1884 431)

The atomic weight of Os has been determined (1) by heating in O and weighing the OsO₄ produced (Berzelius, P 13, 546, Fremy, A Ch [3] 12, 514), (2) by reducing K OsCl₅ in H, washing out KCl, and weighing Os (Berzelius, P 13, 530, Seubert, B 21, 1839, A 261, 257), (3) by determining S H of Os (Regnault, P M [4] 23, 103) The older values were too high Seubert's analyses of K₄OsCl₅ and (NH₄)₂OsCl₆, conducted in 1888, gave the mean value 191 12, but this number was regarded by S as rather too high, in 1891 S re determined the at w very carefully and obtained the value 190 3

Os is distinctly metallic in its physical cha racters, but some of its chemical properties are those of a non metal, eg acidic character of OsO4 and existence of salts the negative radicle of which is OsOs. Os belongs to the group of Pt metals, to which group Cu, Ag, and Au are more or less closely related (v Copper Group or ELEMENTS, 11 250, and Noble METALS, this vol p 628) Os is more closely related to Ru than to the other Pt metals, the analogy is shown in the existence of volatile oxides MO, capable of existing as gases, in the salts K_2MO_4 , and probably KMO, and in other respects. The exist bably KMO,, and in other respects The exist ence of K₂OsO₄, the fact that this salt is oxidised probably to KOsO₄ which salt is re duced to K2OsO, by KOHAq, and also the exist ence of H.OsCy, and salts of this acid, empha sise the analogies between Os on the one hand, and Mn and Fe on the other hand

Detection and Estimation—Compounds of Os heated with a little Na₂CO₃ on Pt foil give the peculiar, chlorine like, odour of OsO₄, at the same time the non-luminous flame becomes luminous from separation of Os Salts of OsO are easily oxidised, e.g. solution of OsCl₂, which is deep blue, becomes violet in air, and then dark red (OsCl₂), and finally yellow (OsCl₄) Salts of Os₂O₃, e.g. K₂OsCl₆, give a brown red pp (Os₂O₄, xH₂O) with KOHAq, a grey brown poil in NH₂Aq, with AgNO₂Aq, and a blue colour (reduction to OsCl₂) on warming with tannic acid. Salts of OsO₂, e.g. K₂OsCl₆, give no pp with KOHAq in the cold, but on warming the liquid goes blue, and then black OSO₂xH₂O

OSMIUM 643

suddenly separates Borax produces no change at ordinary temperatures, but a black pp forms on warming, this distinguishes OsO2 salts from s lts of lrO₂, which become blue on heating with be ax, and after a little give a blue pp Tannic acid does not react in the cold, on warming, the liquid becomes blue Alkalı salts of OsO, form violet solutions in water, HNO, oxidises to salts of OsO, NH,Aq followed by NH,ClAq ppts yel low OsO,(NH, NH,Cl), which gives Os on heating OsO, or OsO,Aq, is recognised by its smell, addition of KOHAq to dilute solutions of OsO, removes the shiell A delicate test for Os consists in fusing with KOH and a little KNO, dis solving K2OsO4 formed in water, adding NH4Cl, washing the yellow pp of OsO₂(NH, NH, Ol)₂ with very dilute HClAq, dissolving it in slightly warm water, and adding K, FeCy₆Aq, when a splendid violet colour is produced (Gibbs, Am Os is usually estimated as the metal Os is separated from other metals by dissolving in aqua regia, adding HNO, and distilling OsO, may be led into excess of NH3Aq, the solution is saturated with H.S and boiled, the pp of OsS₂ is collected, washed, dried, and placed in a small carbon crucible which is placed inside a Hessian crucible, the space between being filled with sand, and heated for some hours to c 220°-250°, compact Os is thus obtained

References — Tennant, T 1804 411 Ber zelius, P 13, 435, 527, 15, 208 Wöhler, P 31, 161 Claus a Jacobi, J pr 85, 142, 90, 65, A 63, 355 Deville a Debray, A Ch [3] 56, 393 Fremy, A Ch [3] 12, 522, 44, 391 Fritzsche a Struce, J pr 41, 97

Osmium, acids of No oxyacid of Os has been isolated, but salts of the hypothetical acids H_2OsO_4 and $HOsO_4$ are known (v Osmium, salts of oxyacids of, p 646) A peculiar acid, $H_1N_2Os_2O_6$, generally known as Osmiamic acid, exists (v Osmium, nitrogen containing acid of, p 644) Osmocyanhydric acid, H_1OsCy_6 , and salts of this acid have been obtained (v Cyanides, vol ii p 343) Salts of the hypothetical acids H_1OsCl_6 and H_1OsCl_6 are known (v Osmium, chlorides of, p 644)

Osmium, alloys of Alloys with copper and gold were described by Tennant (T 1864 411) as very ductile, insoluble in aqua regua An amalgam with mercury is obtained by the reaction of Hg with OsO, Aq (v Claus, J pr 90, 65) The alloy with vidium occurs native, composition varies between c Os, Ir and OsIr, this alloy usually contains Ru, Rh, and Au, besides Os and Ir (v Iridium, Alloys of, this vol p 47) Alloys of Os and Ir were obtained by Deville by melting Os and Ir with Cu, S, and treating the fused mass with HClAq and then with HNO, Aq (M S 1882 1228)

Osmium, ammonio-salts of, or Osm ammonium salts (Ammoniacal osmium bases) Not many of these compounds have been prepared Those which are known seem best looked on as two or more NH₄ groups with H replaced by the radicle OsO or OsO₂. The constitutional formulæ and the nomenclature of the osm ammonium salts are not settled, in this article compounds supposed to contain the radicle OsO are called Osmosyl-ammonium compounds, and those supposed to contain the radicle OsO₂ are called

Osmyl ammonium compounds (after the analogy of NO and NO₂ compounds)

OSMOSYL DIAMMONIUM HYDROXIDE

OsO(NH₁ OH)₂ (Ammonated oxyosmous hydroxide Oxyosmiumammonium hydroxide) Simplest empirical formula = OsO₂ 2NH₃ H₂O Obtained by dissolving OsO₄ in excess of conc NH₃Aq, and warming the red solution in a closed flask to 40°-60° until a black pp begins to form when the flask is opened (Claus a Jacobi, J pr 79, 28) N escapes during the process (330SO₄+10NH₂)

(73OsO₄+10NH₂ = 80sO(NH₂OH)₂+2N₂+3H₂O) Forms a brown black powder, decomposed by heat to Os with evolution of N and H₂O, insol water, sol acids, and reppd by KOHAq or NH₂Aq Amorphous basic salts (not fully examined) are obtained by evaporating the acid solutions, these salts are decomposed by water to neutral and more basic salts (Claus a Jacobi, J pr 90, 65, cf Berzelius, P 13, 435, 527) The base dissolves in KOHAq, on boiling, NH₂ is evolved and a pp, OsO₂xH₂O containing NH₂, separates

OSMYL TETRAMMONIUM HYDROXIDE OsO₂(NH₈ NH₈ OH)₂Aq (Ammoniated oxyosmic hydroxide Osmidiammonium hydroxide Oxyosmiumdiammonium hydroxide Osmulditetramine hydroxide) Simplest empirical formula = OsO₃ 4NH₃ H₂OAq Known only in solution A solution of this base is obtained by decomposing the chloride by Ag₂O and H₂O, or the sulphate by BaOAq (v infra), and filtering, the solution is yellow, has an alkaline reaction, and is easily decomposed with formation of OsO, NH₂, and a black pp (Claus, J pr 79, 28)

OSN2I. TETRAMMONIUM CHLORIDE
OSO2(NH, NH₄Cl)₂ (Oxyosmumdiammonium chloride) The formula is sometimes written
OSO2Cl₂4NH₃, and the salt is called ammoniated osmium oxychloride, the formula is also written
OSO24NH₄Cl₂, and the salt is called osmyl ditetramine chloride (Gibbs, Am 3, 233), Fremy
(A Ch [3] 12, 522) wrote the formula
OSO₂(NH₂), 2NH₄Cl₂ calling the salt osmiamide-ammonium chloride, Claus and Jacobi (J pr
79, 28, 85, 142, 90, 65) gave the formula
OS(NH₃), Ol₂2H₄O, and the name osmio diammonio chloride The investigations of Gibbs (Am.
3, 233) confirmed the empirical formula
OSO₂Cl₂4NH₃ Obtained as a yellow crystalline
pp by adding NH₂Cl to K₂OSO₂Aq (Fremy, A Ch.
[3] 12, 522) (?K₂OSO₄Aq+4NH₄Cl
=OSO₂(NH₃NH₄Cl)₂+2KClAq+2H₂O) Slightly
sol cold water, more sol hot water, insol
NH₄OlAq May be crystallised from water on

= OSO₂(NH₂ NH₃Ol)₂+2RClAq+2H₂O) Signtly sol cold water, more sol hot water, insol NH₄ClAq May be crystallised from water containing HCl, ppd from solution by cone HClAq Aqueous solution quickly decomposes, giving off OSO₄, on evaporation a brown solid is obtained, which behaves like OsO(NH₂ OH)₂, the solution gives a fine violet colour with K₂FeOy₂Aq (Gibbs, Ic) The compound is decomposed by heat, giving a residue of Os

The chloroplatinate is obtained, as orangeyellow crystals, slightly sol cold water, by boiling OsO₂(NH₂,NH₂Cl)₂ with PtCl,Aq (Gibbs, lc)

OSMYL TETRAMMONIUM SULPHATE, NITBATE, &c.
The sulphate is obtained by pouring K.OSO.Aq into cone cold (NH.).SO.Aq, small orange-yellow crystals, easily sol hot water (Gibbs, lc)
The metate is obtained by a similar reaction, and the oxalate also, using cold cone NH.NO.Aq

тт2

644 OSMIUM.

and (NH₄), C₂O₄Aq instead of (NH₄), SO₄Aq (Gibbs,

Osmium, chlorides of. Two chlorides of Os have been prepared, OsCl, and OsCl, OsCl, is known in solution, no chloride has yet been gasified, these are the only haloid compounds. of Os known at present, except OsCy, be classed as a haloid compound OsCl, and OsCl, combine with alkali chlorides to form OsCl, 2MCl and OsCl, 2MCl respectively, OsCl, also probably forms double salts, but they have not been isolated satisfactorily OsCy, forms an acid, H₄OsCy₆, from which various salts (osmocyanides) are obtained OsCl, and OsCl, are formed by direct union of Cl with Os

OSMOUS CHLORIDE OSCI, (Osmium dichloride mosochloride) Obtained by heating finely Osmosochloride) divided Os in a long tube in a stream of dry Cl Two sublimates are obtained, the less volatile (green) is OsCl2, the more volatile (red) is OsCl4 As thus prepared OsCl, forms dark green de liquescent needles, which probably contain H₂O, by heating again in perfectly dry Cl, OsCl₂ is obtained free from moisture as a nearly black sublimate (Claus a Jacobi, J pr 90, 65) indigo-blue solution of OsCl, may be prepared by dissolving OsC.xH₂O in HClAq, the solution soon becomes violet, then dark red, and then yellow from formation of OsCl, and OsCl, the yellow solution again becomes blue by the action of reducers (C a J, lc) OsCl₂ dissolves in water, forming a green liquid, which is decolourused and decomposed on dilution with formation of Os, OsO₄Aq, and HClAq Solutions of OsCl₄ in alkali chloride solutions are not decomposed by dilution, double salts are probably present (O a J) Berzelius said that double salts of OsCl₂ are formed by the action of alcohol on the salts M₂OsCl₄ and M₄OsCl₄ (P 13, 435, 527)
OsCl₂ is sol alcohol and ether The aqueous solution conducts electricity, but the alcoholic and ethereal solutions do not (v Hampe, Z 11, 1549, 12, 23)

OSMOSO-OSMIC CHLORIDE OSCI, (Osmium trichloride Osmochloride Osmium sesquichloride) This chloride is only known in solution, and in combination with alkali chlorides The brown to purple solution obtained by the action of air on OsO.xH.O in HClAq probably contains OsCl. (C a J) By treating a solution of OsO, in HOlAq with Hg, and evaporating in vacuo over cone H.SO., Berzelius (P 13, 435, 527) obtained a purple, varnish-like substance, which perhaps

was OsCl

Double Salts.—Ammonium-osmium tri

chlorade (Ammonium chlorosmite)
2(OsCl, 2NH,Cl) 3H₂O Reddish-brown crystals,
obtained by passing H₂S into OsO, in much HClAq till the solution is red, adding NH Cl, and evaporating (Claus, J pr 79, 28) The salt dissolves in water with a dark purple colour, which is unchanged by addition of alkali, but reduction begins on warming On heating, Os and NH₄Cl are formed (Berzelius, l.c)

Potassium-osmium trichloride chlorosmite) 2(OsCl₂ 3KCl) 6H₂O. (Potassium Formed by strongly heating in Cl a mixture of equal parts KCl and powdered Os, dissolving in water, erystallising out K2OsOl, and evaporating the mother-liquor, also by dissolving KOH in cone OsO, Aq, adding NH, Aq, and when the solution

18 yellow and before K2OsO4 separates, saturating with HOlAq and evaporating to dryness on a water-bath, when the salt is obtained on the bottom of the basin, while KOl and NH Ol and deposited on the upper parts. Forms dick brownish red crystals, easily sol water, with deep cherry-red colour, easily sol alcohol, insol. ether The salt loses 8H₂O in air, and the rest at 150°-180° The aqueous solution easily decomposes with separation of Os_xO_vCl_x

OSMIC CHLORIDE OSCI, (Osmium tetrachloride Osmichloride) Obtained, as a dark red powder, by heating finely powdered Os in dry Cl, OsCl, is formed at the same time OsCl, is the more volatile of the two chlorides In presence of moisture, becomes cinnabar red, and then forms yellow needles (? OsCl, xH₂O) Dissolves in a little water to form a yellow solution, which is decomposed and decolourised on dilution (Berzelius, lc) OsCl, is a non conductor of elec tricity (Hampe, Z 11, 1549, 12, 23) OsO₂ 2H₂O dissolves in conc HClAq, forming a dark greenish brown solution, which probably con

tains OsCl

Double salts -Potassium osmium tetra-(Potassium chlorosmate) K208Cl chloride(=OsCl, 2KCl) Obtained by heating an inti-mate mixture of equal parts KCl and finely powdered Os in dry Cl to low redness, removing excess of KCl by a little water, dissolving the residue in hot water, and allowing to crystallise (Berzelius, lc) Claus a Jacobi (lc) obtained the salt by adding KCl to OsO, in HClAq, then adding alcohol and evaporating lustrous octahedra, cinnabar red when powdered Sol water, forming a yellow solution, from which alcohol ppts the salt, incompletely, as a red crystalline powder Not decomposed at low redness, but at a higher temperature Os and KCl are formed OsO, is produced by distilling HNO, over K2OsCl (Berzelius, l.c) Is not acted on by SO₂Aq at ordinary temperatures (K₂IrCl_e is reduced) KOHAq does not decompose a cold solution of K₂OsCl_e, but on warming the solution becomes blue, and then suddenly ppts black OsO2.2H2O (Claus, l.c., other reac tions of K2OsClAq are given)

Ammonium chlorosmate, silver chlorosmate, and sodium chlorosmate are described by Claus a Jacobi (J pr 79, 28, 85, 142, 90, 65, A 63,

855)

Supposed compound of Osmium hexachloride Berzelius (P 13, 435, 527, 15, 208) obtained a brown salt, which he sup posed to be a compound of NH₄Cl and OsCl₄, by saturating OsO, with NH,Aq, after a time add ing excess of HClAq, digesting for some days with Hg, filtering, and evaporating According to Claus (lc), the salt is 2(OsCl, 2NH,Cl) 3H,O (v supra, Ammonium-osmium trichloride)

Osmium, cyanide of, OsCy2, and osmocyanhydric acid and its salts, H.OsCy, v Cyanides, vol 11. p 348

Osmium, hydrated oxides or hydroxides of, v. Osmum, oxides and hydrated oxides of,

Osmium, nitride of The brass-yellow substance, obtained by passing H over the pp. produced by adding HNO, to K₂OsO₄Aq, is probably a nitride of Os (Claus, P. 65, 202)

Osmium, nitrogen-containing soid of, and

OSMIUM. 645

ets salts H₂N₂Os₂O, Aq or ? H₂N₂Os₂O, Aq acid is generally known as osmiamic acid An queous solution of this acid is obtained by deor mposing the Ba salt by the equivalent quantity of H,80,Aq, or by treating the moist Ag salt with HClAq, and filtering The clear yellow solution remains unchanged for some days if dilute, but if it be concentrated, OsO4 and a black pp containing Os are formed, and gas is The aqueous solution of the acid evolved evolves CO₂ from carbonates, and decomposes KCl, Zn dissolves in it, with evolution of gas and partial decomposition of the acid The solution is decomposed by acids on warming, with production of OsO₄ (Fritzsche a Struve, J pr 41, 97) F a S gave the formula H₂N₂Os₂O₅, this was upheld by Claus (J pr 90, 65) Gerhardt (J Ph [3] 12, 304) gave the formula $H_2N_2Os_2O_4$ The K salt is obtained by the action of NH₃Aq on OsO₄ in excess of KOHAq, the reaction is expressed thus by F a S $2080_4 + 2NH_4 + Aq = H_2N_2O8_2O_4Aq + O + 2H_2O$, Claus gives the equation $608O_4 + 8NH_3 + Aq$ $= 8H_2Os_2N_2O_3Aq + N_2 + 9H_2O$ According to F s S no gas is evolved during the reaction this is correct neither of the equations can express the change which occurs The salts of osmiamic acid explode when heated, some ex plode when struck

K2N2O82O POTASSIUM. OBMIAMATE Prepared by dissolving solid OsO. ? K2N2Os2O in cone KOHAq, to which cone NH, Aq has been added The solution is clear yellow, and deposits yellow crystals of the salt Claus a Jacobi (lc) dissolve KOH in very dilute OsO,Aq, add | vol NH, Aq, and evaporate rapidly until the salt begins to crystallise out, after which crystallisation is allowed to proceed Citron yellow, tetragonal crystals Sol warm water, also in alcohol, sl sol cold water, insol ether plodes at c 180° Decomposed by cone HC Decomposed by cone HClAq, with evolution of Cl and formation of two kinds

of red crystals (v F a S, lc)
SILVER OSMIAMATE Ag₂N₂Os₂O₄ or? Ag₂N₂Os₂O₅

SILVER OSMIAMATE Ag₂N₂Os₂O₄ or? Ag₂N₂Os₂O₅

Red or set of the company of the com A citron yellow crystalline powder, al sol water or dilute HNO,Aq, sol NH,Aq, forming therewith a crystalline compound, blackens in light, explodes at 80°, also when struck by a hammer Prepared by dissolving OsO, in an ammoniacal solution of a salt of Ag, and adding excess of HNO, Aq, or by adding excess of HNO, Aq, fol lowed by solution of a salt of Ag, to OsO, dissolved in NH,Aq

Ammonium, barium, mercurous, sodium, and ammoniated sinc, osmiamates have been pre-

pared (F a. S, lc)

Osmium, oxides and hydrated oxides of Four oxides of Os are known, OsO, Os₂O₂, OsO, and OsO, Salts in which OsO, acts as the negative radicle have been prepared (v infra, Osmium, salts of oxyacids of) A hydrate of OsO has been obtained, but not pure, it rapidly absorbs O, the hydrate OsO, 3H,O is known, as are also the hydrates OsO₃.H₂O and No oxy-salts have been obtained OsO,.2H,O directly from the oxides of Os, a few oxy salts corresponding with OsO are known OsO, acts as a weak acidic anhydride, this oxide is easily reduced to OsO, or to Os OsO, is the only oxide prepared by the direct union of Os with O Chlorides corresponding with OsO and OsO, in HOlAq, HNO, Aq, or H, SO, Aq, oxidation begins

have been obtained, and the chloride OsCl, which corresponds with Os2Os probably exists in solution (v Osmium, chlorides of, p 644)

OSMOUS OXIDE OSO (Osmium monoxide). A greyish black solid, insol acids, obtained by heating in a stream of CO₂ a mixture of Na₂CO₃ and OsSO₃ or OsSO₄ 2K₂SO₄ 2KHSO₄ 4H₂O₇ and washing the residue with water (Claus a Jacobi, J pr 85, 142, 90, 65) The salt OsSO 1s formed by evaporating OsO Aq with excess of SO, the salt OsSO, 2K, SO, 2KHSO, 4H,O is formed by heating K2OsCl.Aq with K2SO2, and washing with water the powder which separates Hydrated osmous oxide, OsO xH2O, was obtained by C a J by the action of warm, very cone KOHAq on OsSO, in absence of air, it forms a blue black pp which very rapidly absorbs O from the air Berzelius obtained a greenish black pp by boiling OsCl₂ in KClAq with KOHAq, this pp was sup-posed to be OsO.xH₂O, but C a J say it cannot be washed free from alkalı A few salts are known corresponding with OsO, eg OsSO, but none is obtained directly from the oxide

Osmo osmio oxide Os2O3 (Osmium sesquioxide) A black powder, insol acids Obtained by gently heating, in a stream of CO_2 , a mixture of K₃OsCl₆ 3H₂O and Na₂CO₃, and wash ing with water (C a J, lc) Deville a Debray (C R 82, 1076) say that this oxide is often formed, as copper red crusts, in the preparation of Os, by passing OsO, vapour mixed with N through a hot tube lined with C, the lining of C being formed by passing C₅H₆ vapour through the tube heated to redness Berzelius supposed that a compound of Os.O. with NH, was formed by the action of NH,Aq on OsO,Aq, but the pp thus formed was shown by C a J to be OsO(NH, OH)₂ (v Osmosyl drammonium hydroxide, p 643) No oxy- salts are known corresponding with Os2O3, a solution of OsCl, has

been prepared

Hydratedosmo - osmic Os, 0, 3H,O, a brown red pp, somewhat sol. cold KOHAq, sol acids even after drying, obtained by adding KOHAq to K,OsCl,Aq (C a J.,

OBMIC OXIDE OSO, (Osmum dioxids) Obtained by Berzelius (P 13, 435, 527, 15, 208) by heating a mixture of K₂OsCl₈ and Na₂CO₃ in CO₂, washing the residue with water, and then with HClAq, as thus prepared OsO₂ forms a greyish-black powder Claus a Jacobi (*lc*) obtained OsO, in the form of a copper red, metal-like solid, by strongly heating OsO, 2H₂O in a covered crucible (OsO, H, and H,O are also formed) OsO, 2H,O is obtained by the action of acids on K₂OsO₄Aq OsO₂ may be heated to redness in absence of air (Berzelius), but Claus save that OsO, and Os are formed Heated in air, or acted on by HNO, and HClAq, OsO, is produced Reduced by H at ordinary temperatures Detonates when heated with combustible bodies. A sulphate corresponding with OsO₂ is said to be prepared by the action of cold HNO.Aq on OsB, but little is known of its properties. The corresponding chloride, OsCl, is known

Hydrated osmic oxide 080, 2H,0, black pp obtained by adding very dilute H_8O,Aq to K_0sO,Aq, OsO, being formed at the same time (C. a. J. l.e.) The moist hydrate dissolves 646 OSMIUM

very quickly, with change of colour from purple to yellow-brown, green, and brownish-yellow on heating From the solution in HClAq, Zn ppts Os (Wöhler, A 140, 256) By heating OsO₂2H₂O to 200° in dry N, Fremy obtained the hydrate OsO₂ H₂O (A Ch [3] 12, 515)

OSMIUM TETROXIDE OsO, (Perosmic anhy Often called perosmic acid, and formerly generally known as osmic acid) Mol w 254 84 VD 1285 at c 280° (Deville a Debray, C R 82, 1076)

Formation -1 By heating Os in air or O 2 By heating Os, or any of the lower oxides, with HNO₃ or aqua regia —3 By the action of dilute acids on K₂OsO₄Aq, OsO₂2H₂O being formed at the same time —4 According to Claus (J pr 79, 28) by the action of Os on steam, H being evolved

Preparation —1 Finely powdered Os is gently warmed in a stream of dry O, the Os is placed in one bulb of a two bulbed tube, and the OsO, condenses in the second bulb -2 Three parts osm iridium are fused with 1 part KNO, the cold mass is dissolved in water, the solution is neutralised by H2SO4Aq, and OsO4 is distilled off into a cold receiver

Properties -Long, colourless, translucent, monoclinic, needles (Mallet, Am S [2] 29, 49) Melts considerably under 100°, and boils a few degrees above its melting point OsO, is very volatile, the vapour smells abominably, and is extremely poisonous, attacking the eyes and lungs, Deville nearly lost his eyesight while working with OsO, (v D a D, A Ch [3] 56, Claus says the best antidote is H2S gas 400) Claus says the best antidote is H₂S gas The VD was determined by D a D at 246°-285°, it agrees with the formula OsO, may be vapourised in H, if the mixed vapours are passed through a hot tube, Os is deposited OsO4 is slowly dissolved by water, the solution does not react acid, sol alcohol or ether, solu tions are reduced with ppn of Os

Reactions -1 Reduced to Os by heating with hydrogen, also by heating in a gas flame, an aqueous solution of OsO, is readily reduced by most metals, the solution is also reduced by phosphorus, ferrous sulphate, stannous chloride, sulphurous acid (a blue liquid is produced by SO, Aq, perhaps containing an oxide which has not been isolated), and by many carbon com pounds (e g H.CO.H., tannin, sugar, alcohol, &c) (v Tennant, T 1804 411, Berzelius, P. 13, 435, 327, 15, 208, Döbereiner a Weiss, A 14, 17, 251, Butlerow, A 84, 278, Claus a Jacobi, J pr 90, 65)—2 A large excess of ammonia solution evolves N, and ppts OsO(NH, OH); (v Osmosyl diammonium hydroxide, p 643) -OsO4 dissolves in potash, forming a red yellow liquid which probably contains K perosmate (q v under Osmium, salts of oxyacids of, infra) —4 Hydrogen sulphide ppts an oxysulphide (q v) from OsO₄Aq, on saturating OsO₄Aq with H₂S, and adding an acid, OsS₄ is ppd (v Osmrum, sulphides of, p 647) -5 Hydrochloric acid does not react with OsO₄, but on addition of KOHAq, K2OsCl is produced. OsO, is a very weak acidic anhydride. an aqueous solution does not affect the colour of litmus, nor does it decompose carbonates; KOHAq probably forms K perosmate.

Osmium, oxyacids of No oxyacid of Os has been isolated, salts of the hypothetical H2OsO4 (osmates) are known, and some of the reactions, of OsO, indicate the existence of unstable salt derived from the oxide OsO, (v infra, Osmiv'n, salts of oxyacids of)

Osmium, oxychloride of The black pp obtained by boiling dilute K₂OsCl₈Aq is probably an oxychloride (Claus a Jacobi, J pr 90, 65)

Osmium, oxysulphides of The pp obtained by passing H2S into OsO,Aq is said by von Meyer to have the composition Os,O,S, 3H,O,

and to be changed to 2080.83 H.0 by the action of air (J pr [2] 16, 77) Dried at $180^{\circ}-200^{\circ}$, 080.8 is obtained (von M, lc)

Osmium, phosphide of A phosphide of Os is said to be formed by heating Os in P vapour, it appears black if prepared at a moderate tem perature, but white and metal like if produced by heating strongly, it burns in air to OsO. and osmous phosphate (Berzelius, P 13, 435,

527, 15, 208)

Osmium, salts of Very few salts have been obtained by replacing the H of oxyacids by Os Osmium sulphite, OsSO3, is formed by evapora ting OsO,Aq with SO.Aq, a complex salt OsSO, 2K,SO, 2KHSO, 4H,O is obtained by heating K,OsCl, with K,SO,Aq, osmous phos phate and sulphate are also said to exist, but they have not been analysed (Berzelius) osmic sulphate is stated to be produced by the action of cold HNO, Aq on OsS, (Berzelius) No salt of Os has been formed by the direct reaction of Os or any of its oxides with an oxyacid (v SULPHITES, SULPHATES)

Osmium, salts of oxyacids of Some salts of the hypothetical osmic acid, H2OsO4, have been isolated, and there are indications of the existence of alkali perosmates, te salts derivable

from OsO4

OSMATES M' OSO (formerly called Osmites) Neither the acid H₂OSO, nor the anhydride OSO, has been isolated (cf Mallet, Am S [2] 29, 49) Alkalı osmates are obtained by the reducing action of alcohol on OsO, in KOHAq, a Ba salt is formed by the prolonged reaction of warm BaOAq on OsO, in a closed vessel, os mates of Ca, Pb, and Sr are obtained as insoluble

pps from the alkalı salts Potassium osmate K₂OsO₄2H₂O violet coloured, crystalline pp of this composi tion is formed by adding alcohol to OsO4 dis solved in KOHAq, the solution is red, then be comes colourless, and deposits the salt Fremy obtained the salt in large octahedra by adding KNO2Aq to OsO4 in large excess of KOHAq (J pr 33, 411) According to Claus (J pr 34, 173, 424) K,OsO, 2H,O is obtained by warming OsO, in an excess of KOHAq, this reaction is similar to the reduction of KMnO,Aq to K2MnO4Aq by KOH Violet red octahedra Sol water, insol alcohol or ether, slightly sol conc salt solutions (Gibbs, Am S [2] 31, 70) An aqueous solution decomposes rapidly on warming to K perosmate and OsO₂xH₂O. H₂SO₄Aq forms OsO₄ from K₂OsO₄Aq, and separates OsO, xH2O (Claus a Jacobi, lc) HNO, Aq produces a similar change (Fremy, lc) SO₂Aq produces a blue solution NH₄ClAq forms produces a blue solution OsO₂(NH₂ NH₃Cl)₃, and (NH₃)₂SO₄Aq produces OsO₂(NH₃ NH₃)₂SO₄ (v Osmyl-tetrammonium chlorids and sulphate, p 643) NH₂Aq is said to form OsO₂(NH₂)₂ (Fremy, l c)

Barrum osmate BaOsO, H.O (Claus, J pr. 4, 17., 224), Calcrum, lead, sodrum, and strontrum osmates have been obtained

(Fremy, J pr 33, 411)

Perosmates (formerly called osmates) These salts have not been prepared pure (J pr 33, 409) says a perosmate of K is formed by dissolving OsO, in large excess of KOHAq, and the salt is decomposed on dilution, the solution in excess of KOHAq is colourless, but absorbs O at d becomes brown, on boiling, K_2OsO_4 is formed, and an oxide of Os containing more O than OsO₄ is volatilised On the other hand, Claus (J pr 85, 142, 90, 65) says that the greater part of the OsO, can be distilled off from a solution of this oxide in excess of KOHAq, but that some decomposes to K2OsO4Aq and O Claus also says that OsO, distils off, at 60°, when Cl is passed into OsO, xH₂O suspended in a large excess of KOHAq From a conc solution of OsO, in KOHAq, HNO,Aq ppts OsO, mixed with OsO, xH₂O, according to Wöhler (A 140, 256) Wohler (lc) melted Os with KOH and KNO, and obtained a black solid which formed a deep red solution in water tion was supposed by Wohler to contain K per osmate, only a very little OsO, was obtained by distilling, and the residual liquid deposited K₂OsO₄ on cooling The mother liquor from the K2OsO4 was yellow, on treatment with CO2 it became colourless, and then violet, and deposited

OsO, and a greyish violet pp
Osmium, sulphides of A sulphide of Os is
formed by heating Os with S (Beizelius, P 13,

435 527, 15, 208)

OSMIC SULPHIDE OSS (Osmium disulphide) A dark brownish yellow solid, slightly soluble in water Produced, according to Fremy (J pr. 83, 409), by passing H₂S into K₂OSO₄Aq, according to Claus (J pr. 79, 28), also by passing H₂S into K OSCl₄Aq

OSMIUM TETRASULPHIDE OSS, xH₂O Obtained by saturating OSO₄ in HClAq with H.S., on attempting to dry the pp it is partly oxidised, above 100°, the pp burns to OSO₄ and SO₂, easily oxidised by HNO₄Aq, heated in absence of air, OsS OSS₂ is said to be produced (Berzelus, Claus) The pp obtained by passing H₂S into OsO₄Aq is an oxysulphide (q v)

M M P M
OSMOCYANIDES and Osmocyanhydric acid

v Cyanides, vol 11 p 343

OSMOSE When two liquids are separated by the intervention of a porous diaphragm, a flow of liquid takes place from one side of the septum to the other, or sometimes an unequal flow of the two liquids in opposite directions, so that the quantity of liquid increases on one side of the septum and diminishes on the other This phenomenon was originally designated by the correlative terms Endosmose and Exosmose, but it is better expressed by the shorter word Osmose (from &oµos, impulsion), which includes the two former For the application of osmotic methods to chemical questions v. Molecular weights, p 417, also Physical methods section Electrical methods

OSOTRIAZOLE C.H.N. L. NH N CH

[22 5°] (204°) at 715 mm Formed by heating its carboxylic acid Sol water and alcohol, msol ligroin (Pechmann, A 262, 320)—B'HCl—B'HgCl glittering needles

Benzoyl derivative NBz < N CH [100°] OSOTRIAZOLE CARBOXYLIC ACID

NH<\(N CH \) CO₂H [211°] Formed by the action of KMnO₄on amide phenyl esotriazele carboxylic acid, which is got by reducing the nitro- acid formed by nitrating the acid produced by the action of soda on the phenyl-hydrazide of dintrose acetone (Pechmann, A 262, 315) Crys talline powder, v sol boiling water —CaA', 2aq

OSOTRIAZONES and OSOTETRAZONES v

OSSEIN v PROTEIDS, Appendix C

OSTRUTHIN C, H,O, 2 (Gorup-Besanez, A 183, 321), C₁₈H₂₀O₃ (Jassoy, C C 1890 [1] 766) [115°] Occurs in the roots of Imperatoria Ostruthium Triclinic crystals, v sl sol boling water, v sol slochol and ether Its alcoholic solution exhibits blue fluorescence Forms a crystalline compound with dry HCl

Acetyl derivative [78°] Plates

OTOBITE C₂₄H₂₂O₄ [133°] Occurs in the fruit of *Myristica otoba* (Uricoechea, A 91, 370) Pearly prisms (from ether), insol water

370) Pearly prisms (from ether), insol water OVABAIN C_{sc}H_{cb}O₁₂ [o 185°] S 65 at 11°, S (alcohol) 3 75 at 11° [a]_n = -33° A poisonous glucoside present in Ouabaio root, used as arrow poison, and in the seeds of the glabrous Strophantus of Gabon (Arnaud, C R 106, 1011, 107, 348, 1162, Bl [3] 1, 10) Rectangular plates (containing 7aq) v sl sol water Its solution is ppd by tannin It yields a sugar and a resin on boiling with acids—BaA' deliquescent pp

OXALACETIC ACID C.H.O. Oxaloxyl

acetic acid

Oxim CO,H C(NOH) CH, CO,H [125°] Formed by the action of alcoholic NaOH on the ether CO.Et C(NOH) CH, CO,H [107°], which is obtained by the action of water on the dihydride of di nitroso di oxy terephthalic ether (Cramer, B 24, 1204) An isomeric oxim CO,Et C(NOH) CH, CO,H [54°] is formed from oxalacetic acid and hydroxylamine It yields CO,H C(NOH) CH, CO,H [88°], whence AcCl forms an anhydride C,H,O, [105°] yielding C,H,AcO, [105°]

Phenylhydrasids of the methyl ether CO₂Me CH₂ C(N₂HPh) CO₂Me [118°] Mol. w 257 (obs), (calc 250) Formed from di methyl accetylene dicarboxylate and phenyl-hydrazine (Buchner, B 22, 2930) Plates Yields oxyphenyl pyrazole carboxylic acid on saponifica

Mono sthyl sther CO,Et CH, CO CO,H [97°] Obtained from the di ethyl ether and cold dilute KOH (Wishcenus, B 19, 3226, A 246, 328) Needles, v sol water Its aqueous solution is coloured deep red by FeCl.

Analide of the ethyl ether

Oo_Et CO CH_OO NHPh [88°] Formed from
oxalic ether, acetanilide, and NaOEt (Wislicenus
a. Sattler, B 24, 1250) Needles, v sol alcohol
p-Toluide of the ethyl ether [135°]

Ethyl anglide of the ethyl ether CO₂Et CO CH₂ CO NEtPh [69°] Formed from NaOEt, oxalic ether, and NEtAoPh (Wislicenus a Sa⁺⁺ler, B 24, 1254) — Cu(Ci, Hi, NO.), [189°]
De-ethyl ether CO₂Et CH₂ CO CO₂Et

182° at 24 mm) SG $^{485}_{-}$ 1 159 Formed by the action of sodium on an ethereal solution of oxalic and acetic ethers (Wishcenus, B 19, 3225, 20, 3892, A 246, 315) Oil FeCl, colours its alcoholic solution red

Reactions -1 Decomposed by dilute acids into acetic and oxalic acids —2 Dilute (10 p c) H₂SO₄ yields pyruvic acid —3 Sodium forms the compound CO2Et CHNa CO CO2Et, which reacts with alkyl iodides, forming alkyl oxalacetic ethers CO₂Et CHX CO CO₂Et The cop per compound Cu(C₂H₁₁O₅), crystallises from alcohol in green needles [163°] —4 Phenyl hydrasine reacts forming a phenyl-hydrazide CO₂Et CH₂ C(N₂HPh)CO₂Et [78°], crystallising in plates, and forming CO,Et C N2 NPh [182°] on heating -5 Aniline at 0° forms CO₂Et CH₂.C(NPh) CO₂Et (c 200° at 10 mm), which gives no colour with alcoholic FeCl The condensation products include C₁₄H₁₅NO₃ [108°] and C₁₂H₁₁NO₃ [218°] (Wishcenus a Spiro, B 22, 8349)—6 Aqueous KOAc yields CO2Et CH C(CO2H) CH(CO2Et) CO CO2Et, which forms the crystalline salts BaA', 2aq and PbA', (Claisen a Hori, B 24, 124) —7 Its oxim is reduced by sodium amalgam to mono ethyl aspartates CO₂H CH(NH₂) CH₂ CO₂Et [201°] CO.H CH. CH(NH.) CO.Et [165°] (Putti, C C 1888, 68, 1459) —8 Bensamidine hydrochloride and dilute (10 p c) aqueous caustic soda yields CO₂Et CO CH₂CO NH CPh NH [180°] (Pinner, B 22, 1628, 2615)

Reference — Amido-oxaloxyl-agetic agid OXALAMIDO-BENZOIC ACID v CARBOXY-

PHENYL OXAMIC ACID

OXALANTIN C.H., N. O. Formed by reducing alloxanic acid with zinc and HClAq (Limpricht, A 111, 133, cf Schlieper, A 56, 2) Small crystals, sl sol water Decomposed by alkalis into NH, and oxaluric acid

OXALBUTYRIC ETHER

CO₂Et CO CHEt CO₂Et (188° at 20 mm) Formed from exalic ether, butyric ether, and NaOEt (Arnold, A 246, 337) Oil Gives a red colour with FeCl₂

OXALETHYLAMYLINE v ETHYL BUTYL-

GLYOXALINE

OXAL-ETHYL-ETHYLINE v. METHYL-ETHYL-GLYOXALINE

OXALETHYLINE # METHYL ETHYL GLY-OXALINE

OXALETHYLŒNANTHYLINE v. ETHYL HEXYL-GLYOXALINE OXAL ETHYL PROPVILLE v. D. DOVING

OXAL ETHYL PROPYLINE & DI-ETHYL-

0%ALICACID H₂C₂O₄2aq, t s CO₂H CO₂H 2aq or C(OH)₂ C(OH)₃ [187°] (when anhydrous) (Staub a Smtth, B 17, 1742 note) SG (hydrated) ¹⁵⁵/₄ 1 653 (Clarke, Am. 2, 174) S (of H₂C₂O₃) 9 5 at 14 5° (Nichols, C N 22, 14), (of H₂C₂O₃) 5 8 at 10°, 10·2 at 20°, 120 at 90° (Alluard, C R 59, 500), 5 5 at 10°, 8 8 at 20°, 68 8 at 70° S (alcohol) 23 5 at 15° (Burgoin, Bl. [2] 29, 248) 8 (ether) 1 27 at 15° (Miczynski, M. 7, 257) B_{CO} 36 74 (in a 741 pc aqueous solution) (Kanonnikoff, J pr [3] 81, 847). H.C.v 61, 100,

H C p 60,200 H.F 196,800 (Stohmann, J pr. [2] 40, 204), 198,000 (von Rechenberg) S H. (0°-50°) 3359 (Hess, A Ch [2] 35, 410)

Heat of neutralisation 28,100

Occurrence —As acid potassium salt in soryal (Oxalia acetosella and Rumex acetosa) (Savary, A.D. 1773, Wiegler, A.D. 1779), as sodium salt in Salsola and Salcormia, as calcium salt in the root, bark, and leaves of many plants, (often found as crystals, raphiles), in urine, urinary calculi, and in the Malpighian vessels of the caterpillar of Sphinx Convolvuli Calcium oxalate is found also in many lichens, and as the mineral Whewellite Ferrous oxalate occurs in lignite beds, and ammonium oxalate in guano Free oxalic acid occurs in some fungi (e.g. Fistulina hepatica (Hamlet a. Plowright, C. N. 36, 93)

Formation -1 By the oxidising action of fused potash or of nitric acid on alcohol, glycol, sugars, starch, cellulose, citric, tartaric, myristic, and other fatty acids Also by oxidising acetic acid and phenol with alkaline KMnO₄ (Japp, CJProc 4, 91) -2 Ammonium oxalate is among the products of the decomposition of cyanogen by water —3 By heating sodium or potassium formate above 400° (Merz a Weith, B 15, 1507) 4 By the action of NaOEt on di bromo acetic ether -5 By passing CO2 over a mixture of sodium and sand at about 360° (Drechsel, Z [2] 4, 120) -6 By heating C.Cl_e with dry KOH for some days at 220° (Geuther, A 111, 174) C.Cl. with dry KOH at 200° forms oxalate and hydrogen -7 By the spontaneous decomposition of $CH_3 CH(ONO_3) CO_2H(Henry, B 12, 1837) - 8 By$ the action of damp oxygen upon CCl₂ CCl(OMe) (Henry) -9 A product in the preparation of picric acid from phenol (Perkin, C J Proc 4, 91)—10 By oxidising chloranilic acid (Groves, O J Proc 4, 91)—11 A by product in the preparation of nitrous ether (Frickhinger, Ar Ph. [**8**] **24**, 1065)

Preparation -By heating sawdust with a mixture of NaOH and KOH at 240°-250°, the yield being less when NaOH is used alone (Thorn, D P J 210, 24) The product is boiled with water, and the filtrate evaporated Sodium oxalate separates in granules, which are then boiled with milk of lime The calcium salt is then decomposed by H₂SO₄ Oxalic acid may be freed from the last trace of alkaline oxalates by crystallisation from boiling dilute (10 pc) HClAq Octahedral crystals of anhydrous oxalic acid H.C.O. may be obtained by allowing a solution of oxalic acid (1 pt) in warm H2SO4 (12 pts) to stand for some days These crystals take up water (2aq) from the air, and fall to powder (Villiers, O. R. 90, 821, of Riechardt, J. 1864, According to Lescour (C R 104, 1799) dried oxalic acid takes up 2 aq from the air

Estimation—By precipitation as calcium oxalate, followed by conversion into CaCO₂ or CaO, or by titration with KMnO₄ or barytawater

Properties—Large monoclinic crystals (containing 2aq), v sol water and alcohol. Gives off its water of crystallisation at 100°, and, in a few weeks, over H₂SO₄ (Erdmann, J pr 85, 213) Partially sublimes at 150°, but is partly split up into water, CO, and CO₂. Its aqueous solution decomposes slowly in light, but the decomposition of dilute solutions may be prevented by

heating for half an hour at 70° Neubauer (Fr. 9, 892) When a gas is passed through a strong colution of exalic acid at 100° CO, is given off (Carles, C R 71, 226) A 5 pc solution contaking 1 pc of uranium nitrate is rapidly decomposed by sunlight into CO2, formic acid, and CO (Seekamp, A 122, 113) Ammonium oxalate is also decomposed by sunlight, but the oxalates of K, Li, and Na are but slightly affected (Downes a Blunt, Pr 29, 219) Ferric chloride is reduced by oxalic acid in sunlight, and also by heating above 50° (Lemoine, Bl [2] 46, 289) Oxalic acid reduces An and Pt from their salts Oxalic acid expels HCl when heated with dry NaCl CaCl, ppts solutions of alkaline oxalates, the ppd CaC, O, being insol acetic acid and ammonia, but sol HClAq, and immediately reppd. by ammonia

Reactions -1 Heated with glycerin (1 pt) it yields CO2 and formic acid, but when a small quantity of glycerin (1 pt) is used, decomposition takes place at a higher temperature, allyl alcohol being formed from the glycerin Oxalic acid also yields formic acid when distilled with glycol, mannite, dulcite, erythrite, and quercite, but not with sugars (Lorin, C R 77, 129, 363, 84, 1136) -2 On heating with conc H2SO4 or with P.O. it is resolved into water, CO, and CO. 3 PCl, yields CO, CO₂, HCl, and PCCl, PCl, acts in like manner—4 Boiling nitric acid slowly oxidises it to CO₂—5 PbO₂ and MnO₂ rapidly oxidise it in aqueous solution, yielding CO2 and oxidised by rubbing with PbO, great rise of temperature occurring—6 MnO, and dilute H₂SO₄ completely oxidise at to CO₂ KMnO₄ and completely oxidise at to CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at to CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at to CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at the CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at the CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at the CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at the CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at the CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at the CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at the CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at the CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at the CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at the CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at the CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at the CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at the CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at the CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at the CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at the CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at the CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at the CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at the CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at the CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at the CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at the CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at the CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at the CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at the CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at the CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at the CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at the CO₂ KMnO₄ and dilute H₂SO₄ completely oxidise at CrO, also oxidise it -7 Chlorine water and HClO yield HCl and CO2-8 Potash fusion yields hydrogen and a carbonate -9 Liberates Cl, Br, and I when its saturated solution is boiled with KClO₃, KBrO₃, and KIO₃ respectively (Guyard, Bl [2] 31, 299) -10 The copper sinc couple forms small quantities of glycollic acid (Balbiano a Alessi, G 12, 190, cf Plimpton, B. 11, 516) -11 SbCl, in chloroform forms crys tals of Sb₂Cl₈C₂O₄ [149°], which are decomposed by water with formation of oxalic acid (Anschutz a Evans, A 239, 285) -12 Primary alcohols heated with dry oxalic acid yield a mixture of mono- and di alkyl oxalates, on distillation the mono alkyl oxalates split up into CO, and alkyl Secondary alcohols give but little formates alkyl oxalate, while tertiary alcohols are wholly split up by oxalic acid into water and hydrocarbons (Cahours a Demarcay, C R 83, 668, 86, 991)—18 Electrolysis of potassium oxalate yields CO₂ at the positive pole (Burgoin, A Ch. [4] 14, 157) —14 A solution of molybdic acid in oxalic acid yields, on addition of HNO, and evaporating, monoclinic crystals of H₂C₂O₄MoO₂ aq, a b.c = 947 1.1 078, $\beta = 98^{\circ}$ 52' This 'oxalomolybdic acid' yields the salts Ag2O2O4MoO25 BaC.O.MoO., and Na.C.O.MoO. 5aq (Pechard, O R 108, 1058) —15 Ammoniacal cupricoxide at 150° yields (NH₄)₂CO₃ and Cu₂O (Cameneuve, Bl [2] 32, 277)

Salts (Souchay a. Lenssen, A. 99, 31, 100, 808, 102, 35, 41, 103, 808, 105, 245) — K_A"aq monoclinic crystals, a b c = 675 1 1 157, \$\beta = 69 5^\circ\$ (De la Provostaye, A Ch. [3] 4, 454) S. 38 at 16° (Nichols) — K_A"8aq — KHA". Salt of sorrel.

Monoclinic crystals (Marignac, J 1855, 462) -KHA"aq -KHA" aq trimetric crystals, a b c = 459 16 196 S 38 at 8° — KHA" ag trimetric crystals (Rammelsberg, P 93, 24) — KH, A", 2aq. Triclinic prisms $a \ b \ c = 2 \ 100 \ 3 \ 256 \ 1$, $a = 96 \ 12$ ', $\beta = 79^{\circ} 29'$, $\gamma = 97^{\circ} 5'$ (Wollaston, Tr 1808, 99, Anderson, C J 1, 231, De la Provostayo) S 18 at 13° (N) —Na,A" S 3 at 15° Neutral in reaction —NaHA"aq monoclinic crystals which redden litmus S 17 at 15° —Li,A" S 8 at 17° —(NH),A"aq 19 5° —LiHA"aq S 8 at 17° —(NH.),A"aq S 42 at 15° (N), 22 at 0° (Engel, C R 102, 365) Hemihedral efflorescent trimetric prisms, a b c = 776 1 733 (Anschütz, B 18, 1394) Ppd. by adding NH,Cl or NH,OAc to its solution (Heintz, J pr 87, 809) — (NH₄)A" 2aq 0 curs in guano (Tanner, C N 32, 162) – (NH₄)HA" aq trimetric prisms, a b(NH₄)HA"aq trimetric prisms, a b c = 453 1 559 — (NH₄)H₄A"₂2aq triclinic prisms, isomorphous with KH₄A"₂2aq 8 3 25 at 0°(En-gel) — (NH₄)HSO₄H₂C₂O₄ monoclinic crystals. —Rb₄A"aq (Piccard, J pr 86, 449) —RbH₂O₄— BbH₄A"₄3aq (Stolba, G C 1878, 331) —CaA"aq Crystalline powder, formed by ppg hot solu-tions (Schmid, A 97, 225) —CaA" 3aq occurs, myrd with CoA"ac in the professor from the constant mixed with CaA"aq in the pp formed from cold solutions — (CaA", CaCl, 24aq — CaA"CaCl, 7aq (Fritzsche, P 28, 121) — SrA"aq S 5 at 100° — SrA"3aq (Wicke, A 90, 101) — SrH₄A", 2aq — SrA"SrCl₂6aq -(SrA")₃SrCl₂16aq (Ranney, Pr. 14,144) -BaC₂O₄aq S 04 -BaH₂A", 2aq S 3 at 15° (Clapton, C J 5, 223) -Be(NH₂)₄A", 2 (Sénarmont, J 1857, 295, Shadwell, J 1881, 681) —BeK₂A"₂—Be₂K₃A"₂(OH)₂2aq (Philipp, B. 16, 752) —MgA" 2aq S 07 at 16°, 08 at 100°. 16,752) — MgA" 2aq S 07 at 16°, 08 at 10°, — Mg(NH₄)₁₂A", 9aq — Mg₃(NH₄)₂₈A"₁₈ 24aq —
Mg(NH₄)₁₄A", 8aq — Mg(NH₄)₁₄A", 8aq —
Mg(NH₄)₁₄A", 2aq (Brandes, Schw J 27, 18) —
MgK₄A", 6aq — ZnA" 2aq — Zn(NH₄)₁₄A", 3aq
(Kayser, P 60, 140) — ZnK₄A", 4aq — CdA" 8aq
S 008 in the cold, 090 at 100° — CdA"(NH₄)₁₂aq
— Cd(NH₄)₁₄A", 9aq — Cd(NH₄)₁₄A", 11aq
— Cd(NH₄)₁₄A", 8aq — CdK₄A", 2aq
— Al₄A" (OH₄), (Mathieu Plessy, O R 97, 1033)
— Al₄Na₄A", (OH₂9aq (Lenssen, J pr 86, 314)
— Al₄Na₄A", (OH₂9aq — Al₄(NH₄)₂A", (OH₂9aq
— Al₄Na₄A", (OH₂9aq — Al₄Na₄A", (OH₂9aq
— Al₄Na₄A", (OH₂9aq — Al₂Na₄A", (OH₂9aq
— Al₄Na₄A", (OH₂9aq
— Al₄ -Al,Na,A",(OH),9aq (Lensen, J pr 86, 314) Al,(NH),A",(OH),5aq -Al,(NH),A",(OH),3aq Al,Na,A",(OH),6aq - Al,Na,A",(OH),2aq Al,K,A",(OH),2aq - Al,K,A",(OH),2aq Al,MgA",(OH),5aq -Al,Ba,A",(OH),8aq (Collin,
B 3, 315) -Ca,A",9aq (Join, Bl. [2] 21, 540) La,A",9aq (Ciève, Bl. [2] 21, 202) -Tl,A'
(Crookes, O J 17, 150, Kuhlmann, C R 55,
607) -TlHA"aq -Sm,A", 10aq -SmKA", 2, 2aq
(Ciève, Bl. [2] 43, 171) -FeA", 2aq
(Ciève, Bl. [2] 43, 171) -FeA", 2aq

golden
the cold, 026 at 100° -K,FeA", 2aq
golden the cold, 026 at 100° —K.FeA", 2aq golden needles. sol. water — K.FeA", aq — (NH₄)₂FeA''₂8aq — Fe(NH₄)₂A''₂8aq agreement crystals S 48 at 17° — Fe(NH₄)₄A''₂4aq — FeNa₂A''₄4aq — FeK₂A''₃8aq S 7 at 17° — KFeA''₂8aq S 92 at 21° — Ba₂Fe₂A''₄7aq — K₂Cr₂A''₄6aq Deep-blue monoclimic prisms; k_Cr_A'', 5aq Deep-blue monoclinic prisms; obtained by reducing K_Cr_O, with oxalic acid (Gregory, Rammelsberg, P 93, 24, Werner, C J. 83, 404, 602, C J Proc 3, 142, C A Schunck, C N 51, 152, Hartley, C J Proc 3, 4) S 20 at 15°. The solution is red with green reflex, and gives no pp. with CaCl_,—K_Cr_A'', 8aq; red monoclinic crystals (Croft, P M [3] 21, 197) S 10—Na_Cr_A'', 8aq blue prisms.—Na_Cr_A'', 9aq—(NH_0*Cr_A'', 6aq blue scales. S. 75 at 15°—

 $(NH_4)_1Cr_2A''_4$ 8aq· red crystals —Ag_Cr_A''_69aq blue needles S 11 at 100° —Ba_Cr_A''_612aq blue needles S 11 at 100°—Ba,Cr,A'', 12aq dark violet needles—Ba,Cr,A'', 6aq (Werner)—Ba,Cr,A'', 18aq—Ba,Cr,A'', 6aq (Clarke, B 14, 1640)—Ca,Cr,A'', 18aq—Ca,Cr,A'', 36aq (Reece, C R 21, 1116)—Cr,Cl,A'',10NH, (Joigensen, J pr [2] 20, 143, 30, 28)—Cr,A'', 10NH, (Joigensen, J pr [2] 20, 143, 30, 28)—Cr,A'', 3(NH,)1,24aq—KČaCrA'', 4aq Pleochrior, red, blue, and green (Hartley, Pr 21, 499)—K,Ca,Cr,A'', 6aq (Werner) blue prisms—KBaCrA'', 3aq—Sr,Cr,A'', 18aq—KSrCrA'', 5aq—Pb,Cr,A'', 45aq—UrA'' 6aq—UrA'', 6aq—Pb,Cr,A'', 45aq—UrA'' 6aq—UrNH,),A'',—UrO,A''3aq—UrO,(NH,),A'', 24aq—(UrO,)K,A'', 23aq—MnA'' 21aq—S 05 in the cold, 08 at 100°—MnA'' 2aq—Decomposes at 150° into CO,, CO, and MnO (Castelaz, Bl [2] 50, 645)—MnA'' 3aq—S G (of MnA'') 21-4 2 444 50, 645) —MnA" 3aq S G (of MnA") 21.4 2 444

50, 645) —MnA" 3aq S G (of MnA") 6aq black (Clarke, Am 2, 174) — K₈Mn₂A''₆6aq black monoclinic prisms (Kehrmann, B 20, 1594) — Mn(NH₄)₄A''₂2aq — Mn(NH₄)₄A''₄4aq monoclinic prisms (Kehrmann, B 20, 1594) — Mn(NH₄),A''₂ 2aq — Mn(NH₄),A''₃ 8aq — Mn(NH₄),A''₄ 8aq — Mn(NH₄),A''₄ 8aq — Mn(NH₄),A''₄ 8aq — MnA'NH₄,6aq — MnK₂A''₂2aq — CoA'''2aq — Co₄A''(OH), — CoK,A''₄6aq — CoA''Cl 5NH₃ (Krok, J pr [2] 18, 239) — CoA''Br 5NH₄ — Co(O(H)A''(NH₄),SO₃SNH₃ — Co₄A''(NO₂)5NH₃ — CoA''(NO₂)5aq — CoN₁A' (NH₃),4½aq (Rautenberg, A 113, 360) — NhA'' 2aq — NhA'' (NH₃),3aq — (Winkelblech, A 13, 278) — K_NhA''₂ 6aq — CuA''₁Aq — Cu(NH₄),A''₂2aq — CuA''(NH₃),aq — CuA''NH₃ — CuLi,A''₂2aq — CuK₂A''₄4aq — CuNa₂A''₂2aq — DhA'' (Plouze, A Ch [3] 51, 103) — CuK₂A''₂2aq — CuA''₂A''₄aq — CuNa₂A''₂2aq — PbA'' (Plouze, A Ch [2] 79, 104, [3] 4, 104) — Pb₃A''O₂ — Pb₂A''(NO₃)₂2aq pearly plates (Johnston, P M [3] 13, 25, Dujardin, J pr 15, 308) — Pb₆A''(NO₃)₆O₂3aq — PbK₂A''₂2½aq (Reis, B 14, 1174) — Hg,A'' white pp, insol water—Hg₂A'''aq—HgA'' — Pbk_2A"_2 2 aq (Reis, B 14, 1174) — Hig,A" white pp, insol water — Hig,A" aq — HigA" — Hig(NH_1),A"_2 aq — HigK,A" 2 aq — Bi_1A"_3 7 aq — Bi_1A"_2 (OH)_2 aq — Bi(NH_4)_1,A"_3 12 aq — BiK,A"_3 12 aq — BiK,A"_3 12 aq — BiK,A"_3 12 aq — Sb_2K,A"_4 aq — Sb_1K,A"_3 aq — Sb_2K,A"_4 aq — Sb_1K,A"_3 aq — Sb_1K,A"_3 aq — Sb_1K,A"_3 aq — Sb_1K_3A"_3 aq — Sun₃A' 3 2aq (Ray, C N' 51, 195) — Sun₄A'', 4aq (Wagner, Chem Zett 12, 1726) crystalluses also with 1½aq, 4½aq, and 6aq — Sb₂K₂H₄A'', 3aq Sb₂Na₅A'', 9aq (Svenssen) — SbNa₅A'', 10aq — Sb(NH₄)a'', 32aq — Sb(NH₄)A'', 25aq (Svenssen, B 3, 314) — Sb₄(NH₄)a'', 16aq — SbH(NH₄), A'', 7aq — AsK₅A'', 3aq — Pd(NH₄), A'', 2aq (Kane) — Pd(NH₄); A'', 2aq (Clève, Bl. [2] 45, 191) — Pt(NH₄); A'', 2aq — PtNa₂A'', 2aq — PtCaA'', 26½aq — PtCaA'', 24½aq — PtCaA'', 25aq — PtSrA'', 25aq — PtBAA'', 25aq — PtBAA'', 25aq — PtBAA'', 25aq — PtBAA'', 25aq — PtMaA'', 36aq — PtBAA'', 25aq — PtMaA'', 36aq — PtHMaA'', 37aq — PtCAA'', 25aq — PtHMaA'', 35aq — PtA''(NH₄), 1½aq — SnA'' — Sn(NH₄), A''', 3aq — SnA'' — SnA'' — Sn(NH₄), A''', 3aq — SnA'', 35aq — SnA'' — SnA'' — SnA'' — SnA'', 35aq — SnA''', 35aq — SnA'''', 35aq — SnA''', 35aq — SnA'''', 35aq — SnA''', 35aq — SnA'''', 35aq — SnA''', 35aq — SnA'''', 35aq — SnA''', 35aq — SnA'''', 35aq — SnA''', 35aq — SnA'''', 35aq — SnA'''', 35aq — (Wagner, Chem Zert 12, 1726) crystallises also pp -Ag, A"4NH,

Mono methyl ether MeHA" (109° at 12 mm) Solid (Anschütz a Schönfeld, B 19, 1442, A 254, 8) — KMeA" (Salomon, B 8, 1509)

Di-methy l ether Me, A" Mol w 118 [54"] (164") (Dumas a Péligot, A Ch [2] 58, 44, Wöhler, A 81, 876, Erlenmeyer, N Rep Pharm 23, 624, Purdie, C J 51, 629) S V 116 7 H F 180,900 (Stohmann, J pr [2] 40, 353 Monoclinic tables, sol water, alcohol, and ether Its

aqueous solution slowly decomposes into oxalic acid and \mathbf{MeOH}

Tetra-methyl ether CO₂Me C(OMe), (76° at 12 mm) SG ²⁰ 1 1312 Formed from CO₂Me CCl₂(OMe) and NaOMe (Anschütz, 1254, 31) Converted by PCl₃ into Me C₂O₄

Mono ethyl ether EtHA" Ethyloxaho acid (117° at 15 mm) S G $\stackrel{...}{\psi}$ 1 2175 Formed from Et₂C,O₄ (1 mol) and KOH (1 mol) in al cohol (Mitscherlich, P 33, 332) Formed also by heating anhydrous oxalic acid (1 pt) with absolute alcohol (1 pt) at 135°, decanting from unused oxalic acid, and distill ng in vacuo (Anschutz, B 16, 2413, A 254, 9) Liquid When distilled under atmospheric pressure it yields formic acid and Et.O₂O₄—KEtA" scales, decomposed by heat into CO and KEtCO₃ (Elte koff, B 6, 1259)

Die thyl ether Et A" Oxalic ether (186° cor) SG $^{20}_{\circ}$ 10793 μ 14156, R $_{\infty}$ 54 (Bruhl) SV 166 2 (Bruhl, A 203, 27), $^{12}_{\circ}$ 10856, $^{22}_{\circ}$ 10761 (Perkin, C J 45, 508) MM 6 654 at 12 8° SH 45 (R Schiff, G 17, 286) Formed by distilling dehydrated oxalic acid (11 pts) with absolute alcohol (14 pts) (Berg mann, Opuscula, 1 256, Lówig, J pr 83, 129), or by heating kHC O₄ (1 pt) with alcohol (1 pt) and H₂SO₄ (2 pts) (Dumas a Boullay, J Ph 14, 113)

Preparation —Equal weights of dry oxalic acid and alcohol (97 pc) are boiled for 4 hours and distilled, as soon as the thermometer reaches 110° a quantity of alcohol equal to the weight of the distillate is added, and the mix ture boiled again for 4 hours, the mixture is then distilled, 825 g oxalic acid give 750 g (or 56 pc) oxalic ether and 110 g formic ether (Schatzky, J pr [2] 34, 500)

Properties — Colourless oil with slight odour, v sol alcohol Decomposed by water, especially on heating Alcoholic potash yields a pp of KEtCQ, With SnCl₂ it forms crystalline Et₂C₂O₄SnCl₄, decomposed by water (Lewy, C R 21, 371) TiCl₄ yields Et C₂O₄TiCl₄ and Et₂C₂O₄TiCl₄ (Demarçay, C R 70, 1414) Reactions — 1 Gaseous NH₃ yields CO₂Et CONH₂ — 2 Aqueous NH₄ forms oxamilar the constant of the con

Reactions — 1 Gaseous NH, yields CO_Et CONH2 — 2 Aqueous NH, forms oxamide 8 Ethylamine yields C_O_(NHEt), diethyl amine forms CO Et CONEt, while triethyl amine has no action (Hofmann) Alanine forms two compounds C_1H_20N O_8 [127°] and [154°] — 4 Sodium and potassium decompose it, yielding CO and Et_CO_NAOEt acts in the same way (Geuther, Z [2] 4,656) — 5 Sodium-amalgam yields des oxalic ether C_H_3Et_O_8, and, when alcohol is present, tartaric and glycollic acids — 6 ZnEt_1, followed by water, yields CO_2Et CEt_2(OH) (Frankland, Pr 12,396) Other zinc alkyls act in the same way (Frankland a. Duppa, Pr 13, 140, 14, 17, 79, 83, 191) — 7 Acted on by Zn and a mixture of EtI and allyl iodide a mixture of HO CEt_CO Et and HO C(C,H_1), CO_2Et is formed, and not HO CEt(C_3H_3) CO_2Et (Barataeff, J pr [2] 35, 7) 8 Resorcin (1 mol) and NaOEt (2 mols) in alcohol slowly form C_1H_10O_0, which crystallises from alcohol in pale yellow prisms [o 256°], and yields the acetyl derivative C_1H_Ac_O_0, [127°] (Michael, J pr [2] 35, 510) — 9 Phenylhydrazine forms C_2O_2(N_1H_2Ph), [278°] and N_2H_Ph CO CO_2Et [119°] (E Fischer, A 190,

181, Bulow, A 236, 197) In presence of alcoholic NaOEt the product is N₂H₂Ph CO CO₂H [170°] (Michael, J pr [2] 35, 458) —10 Actions in presence of NaOEt (1 pt) in alcohol (60 pts) forms CH, CO CH, CO CO, Et [18°] (214°) This body is converted by baryta water into oxyacid, an intermediate body being CH2Ac C(OH)(CO2H) CHAc CO CO,Et [90°] Acetone (2 mols) and NaOEt (2 mols) in ether yield CH, CO CH, CO CO CH, CO CH, [121°] crystallising in white prisms (Claisen a Stylos, B 20, 2188, 21, 1141, 22, 3271, 24 116) A mixture of acetone, NaOAc, KOAc, and Ac₂O yield a coloured product C₆H₈O₈ Another product of the action of alcoholic NaOEt on acetone and oxalic ether is CO(CH. CO CO2Et), [104°], which yields chelidonic acid on warming with mineral acids On adding sodium to a mix ture of oxalic ether and EtOAc dissolved in Et₂O, oxalacetic ether is formed -11 Succinic ether and NaOEt yield oxalosuccinic ether CO2Et CH(CO CO2Et) CH2.CO2Et and a compound $C_{16}\dot{H}_{22}O_{10}$ [90°] (Wishcenus, B 22, 889) — 12 Alcoholic acetophenone and NaOEt form benzoyl pyruvic acid C₆H₅ CO CH₂ CO CO₂H [158°] Acetophenone and NaOEt in ether yield BzCH, CO CO CH, Bz [180°] (Classen, B 21, 1131) -13 Chloro acetic ether and zinc yield 'ketipic' ether CO.Et CH, CO CO CH, CO.Et [77°] (Fittig a Daimler, B 20, 202) -14 Heat ing with oxalic, formic, or acetic acids at 140° yields formic ether, CO, and CO Benzoic acid has no action even at 240° (Lorin, Bl [2] 49, 344) -15 Benzyl cyanide and NaOEt yield CN CHPh CO CO Et [130°] whence boiling dilute H₂SO₄ forms phenyl pyruvic acid [155°] (Erlen mever B 22, 1483) -16 A solution of urea in alcoholic NaOLt gives a pp of sodium parabanate $\frac{\text{CO NNa}}{\text{CO NH}}$ CO (Michael, J pr [2] 35, 457) — Phthalide and NaOEt in ether yield CH CO CO2Et

C°H' [121°], whence phenyl

hydrazine forms C₁₈H₁₆N₂O₄ [159°] (Wishcenus, A 246, 342)—18 Chlorine in sunlight forms (C,Cl₅) C,O₄ [144°], whence potash yields (C,Cl₅) C,O₄ [144°], whence potash CCl₅ CO₂K (Malaguti, A Ch [2] 74, 299) vields

Tetra-ethyl ether CO,Et C(OEt), at 12 mm) SG ²⁰ 10020 Formed from CO₂Et CCl₂(OEt) and NaOEt (Anschutz, A 254,

Converted by PCl, into Et,CO,

Methylethylether CO Me CO, Et (174°) SG § 11557 SV 1391 (Wiens, A 253, 297) Formed by distilling KEtC.O. with KEtSO. (Chancel, Compt. Chim. 1850, 373, 403), and by the action of MeOH on COCl CO.Et or of EtOH on COCl CO, Me (Paul, C J Proc 2, 168) Con verted by repeated distillation into a mixture of Me,C,O, and Et,C,O,
Di methyl di ethyl ether

CO₂Me C(OMe)(OEt)₂ (92° at 13 mm) Formed from CO₂Me CCl₄(OMe) and NaOEt at 100° (Anschutz, A 254, 35)

D1-methyl d1-ethyl ether
CO_Et C(OEt)(OMe)₂ (96° at 12 mm) Formed
from CO_Et COL₂(OEt) and NaOMe at 100°

n Propylether PrHA" (119° at 13 mm) BG 20 1 1578 Liquid (Anschütz a Schönfeld, B 19, 1442, A 254, 6)

Pr,A" (2135°) Din-propyl ether

S G $\frac{9}{6}$ 10384 S V 2154 (W, cf Cahours, C R 77, 749) S H 451

Tetra-n-propyl ether 7°) SG 2 9566 CO2Pr C(OPr), Formed CO2Pr CCl2(OPr) and NaOPr (A)

Iso propyl ether CO.Pr CO.H (111° at 13 mm) SG 20 11657 Decomposes on bolling into Pr₂C₂O₄, isopropyl formate, CO₂, CO,

nd water (Anschutz, A 254, 6) —CO Pr CO K

D1-200 buty l ether (O,H₂)2A" (225°)
SG 14 1 002 SH 457 Yields K(C,H₂)C₂O₄

(Cahours, C R 77, 1403)

Tetra-isobutyl ether (C₄H₅O)₅C CO₂C₄H₅ (146° at 10 mm) S G 921 Formed from C₄H₅O CCl₂ CO₂C₄H₅ and NaOC₄H₅ (Anschutz, A 254, 33)

Din butyl ether (C,H,),A"

S V 2584 (Wiens) S G 9 1 0099

Isoamyl ether (C,H,)HA" Oil, smelling of bugs (Balard, A Ch [3] 12, 309) -CaA'2 2aq -AgA' pearly scales

Di iso amyl ether (C₃H₁₁),C₂O₄ (SG 11 968 (Delffs, J 1854, 26) SH (Schiff) Oil, smelling of bugs (Balard)

Tetra amyl ether $(\tilde{C}_3H_{11}O)_3C CO_2C_3H_{11}$ (190° at 14 mm) SG 29 9141 (A)

Ethyl heptyl ether CO Et CO₂C,H₁₈ (263 7°) S G ⁶ 9954 S V 284 9 (Wiens) Propyl heptyl ether Pr(C.H₁₅)A" (284°) S G § 9814 S V 315 7

Propyloctyl ether Pr(C₈H₁₇)A"

S G & 9725 S V 340 4 (Wens)

Allyl ether (C,H,),A" (215 5° 1 V) (Kekulé, B 6, 387) S G 15 1055 Formed from Ag,C₂O₄ and allyl iodide (Hofmann a Cahours, A 102, 288)

Di phenyl ether Ph₂C₂O₄ [130°] Formed by heating phenol (1 pt) with dry oxalic acid (1 pt) and POCl₄ (1 pt) at 115° (Nencki, J pr [2] 25, 283) Prisms (from alcohol), sl sol ether

Di phenylortho oxalate (PhO)₂C (OH)₄ [127°] manufacture of aurin A by product in the Formed by distilling phenol with dry oxalic acid, or by dissolving oxalic acid and excess of phenol in HOAc (Claparède a Smith, C J 43, 358, Staub a Smith, B 17, 1740) Thin white plates, distilling with decomposition at 150°-180° Sol water, but Sol water, but almost at once split up into phenol and oxalic acid Alcohol yields phenol and oxalic ether. On heating with H2SO, it yields aurin

Dr (a) naphthylortho oxalate (C₁₀H₇O) C₂(OH), [163°] Formed by heating (a) naphthol with dry oxalic acid and HOAc

Crystalline powder (S a S)

D₁ (β)-naphthylortho oxalate H.O).C.(OH), [167°] White crystalline (C₁₆H₁O)₂O₂(OH), [167°] White crystalline powder (from HOAc), partly decomposed on distillation (Staub a Watson Smith, C J 45,

Penta chloro-ethyl ether CO.H. CO.C.Cl. Formed from CO(NH₂) CO.C.Cl. and NH₂Aq (Malagut, A Ch [2] 74, 308) Colourless deliquescent needles —NH₂A'

Chlorade of the methyl ether CO_Me COCI (120°) SG 20 1 3316 Formed by heating CO.Me CCl2(OMe) for 40 hours at 215°

(Anschutz, A 254, 26) Liquid Chloride of the ethyl ether CO.Et COOl

Chloroxalic ether. Chloro glyoxylic ether (q v) (186°) S G 10 1 2223 PCl, acting upon oxalic

ether first forms CCl₂(OEt) CO₂Et, which may be distilled under 15 mm pressure, when distilled under atmospherio pressure it is split up into EtCl and COCl CO₂Et (Anschutz, B 19, 2158, A 254, 27) Formed also from oxalic 2158, A 254, 27) Formed also from oxalic ether and POCI, (Henry, B 4, 598, 5, 949)
Decomposed by water Alcoholic NH, yields ethyl oxamate Anilne forms CO(NPhH) CO₂Et Mercaptan forms CO₂Et CO SEt (Morley a Saint, C J 48, 400) ZnEt, followed by water forms CEt₄(OH) CO_Et Carbamic ether yields CO_Et NH CO CO_Et [45°] (Salomon, J pr [2] 9, 290) CO(NH₂)CO₂Et at 180° yields [2] 9, 290) CO(N. NH(CO CO₂Et), [67°]

Chlorede of the propyl ether
COCI CO₂Pr (154°) SG ²⁰ 1 1670 Formed
by treating Pr₂C₂O₄ with PCl₃ and heating the
resulting CO₂Pr CCl₂(OPr) at 190° (Anschutz)
Chlorede of the isobutyl ether

COOl CO.C.H. (165°) SG 20 1 1153 Formed ın lıke manner

Chloride of the isoamyl ether
COCl CO₂C₅H₁₁ (185°) S G \$\frac{3}{2}\$ 1 0931 (A)
Oxamic acid CO(NH₂) CO₂H Mol w 89
[210°] S 14 at 14° Formed by heating CO2(NH4) CO2H or by boiling oxamide with aqueous NH, (Balard, A Ch [3] 4, 93, Tous saint, A 120, 237) The NH, salt is also formed by passing NH, into a cold alcoholic solution of exalic ether (De Coppet, A 137, 105 Excreted when animals are fed with oxamic ether Prepared by heating an aqueous solution of CO(NH₂) CO₂Et to boiling, adding ammonia gradually till the liquid is alkaline (Oelkers, B 22, 1566) Prepared also by heating ammonium 22, 1666) Frepared also by heating ammonium oxalate with NH₄NO₂ for four hours at 175° (Mathieu Plessy, C R 109, 653) Crystalline powder, sl sol alcohol Converted by boiling water into (NH₄)HC₂O₄—NH₄A'—NH₄A'1½ aq—NaA'½aq—KA'aq (Engström, J 1856, 453)—MgA'₂8aq—CaA'₂4aq S (of CaA'₂) 16 at 13°, 4 at 10°—BaA'₂3aq—PbA'₂aq—Pb(OH)A'—FeA'₃aq—NiA'₂aq—CuA'₂aq (Bacaloglio, J pr. 81, 869)—AgA' needles

Mathiul sther MeA' Cubes

Methyl ether MeA' Cubes Ethylether CO(NH2) CO2Et Oxamethane [115°] Formed from oxalic ether and dry or alcoholic NH₄ Plates (from alcohol) With COCl CO₂Et it forms (CO₂Et CO)₂NH [67] With cyanic acid vapour at 130° it yields O15H24N6O12 [155°-160°] (Grimaux, Bl [2] 21, 154), crystallising from water in needles. Chloral forms CCl₂ CH(OH) NH C₂O₂Et [121°] (Moscheles, B 24, 1804)

Penta-chloro-ethyl ether C.Cl.A' [184°] Formed from (C,Cl,),C,O, and NH, (Mala-

Isobutyl ether C.H.A' [90°] Prism (Cahours, O. R. 77, 1408, Wallach, B. 18, 507) Isoamylether C.H., A' [93°] Phenyl ether CO(NH,) CO, Ph. [182°]

Formed from CO₂Et CCl₂(NH₂) and phenol

CO(NHAc) CO,Et

Acetyl derivative of the ethyl ether CO(NHAc) CO.Et [54°] Needles
Oxamide CO(NH.) CO(NH.) S 037 at 78° (Henry, C. R 100, 948) H.F 169,000 (Berthelot) Formed from oxalic ether and NH.Aq (Bauhof, A.D 1817) Formed also by heating ammonium oxalate (Dumas, A Ch. [2] 44, 129, 54, 240) and by the slow decomposition of cyanogen by water containing aldehyde (Liebig, 4 118, 246), or by cone HClAq (Schmidt a Glutz, B 1, 66) It also occurs among the products of oxidation of HCy, eyamdes, and ferrocyanides (Playfair, Attfield, C J 16, 94)

Properties — White powder, al sol hot water, insol alcohol Cupric acetate forms the sait

Cu(C,H,N2O2)2 aq

Reactions —1 By passing through a red hot tube it is decomposed into CO, ammonium carbonate, HCy, and urea.—2 P2O, yields, on heat ng, cyanogen, CO, and CO—8 Boiling drlute acids yield oxalic acid—4 Boiling agueous alkalis also saponify it Magnesia acts in the same way [Berthelot, BI [2] 47, 840)—5 Water at 224° forms ammonium oxalate -6 Heating with HgO yields urea, CO2, and Hg (Williamson) Boiling with water and HgO forms a compound (C₂H₄N₂O₂)₂HgO (Dessaignes, A 82, 233) —7
Ac₂O has no action at 160° Bz₂O at 200° forms benzamide —8 Cone HNO, decomposes it in the cold

Oxalimide CO>NH Formed from oxamic acid, PCl, and POCl, at 80°-90° (Ost a Meute, B 19, 3228) Monoclinic prisms, v sl sol cold water, sol NH, Aq Boiling water produces oxamide and oxalic acid —C₂O₂NHgCl crystal line powder, insol water

Methyl oxamic acid CO(NHMe) CO₂H [146°] (Hantzsch, B 17, 2919) Formed by heating methylamine acid oxalate (Wurtz, A Ch [3] 30, 443), and, as a subsidiary product, by oxidising caffeine with CrO, (Maly a Hinteregger, M 2, 128) Crystals (from hot water or by sublima tion) — KA' — CaA'₂— CaA'₂3aq — BaA'₂aq a b c = 101811306monoclinic crystals, $B = 87^{\circ} 13'$

Methyl ether MeA' [85°] Formed from Me₂C₂O₄ (76 g) and methylamine (20 g) in MeOH (30 g) (Franchimont a Klobbie, R T C 8, 305) Ethylether EtA' (243°) Oil

Methyl oxamide CO(NH₂) CO(NHMe) [229° Formed from oxamic ether and NMeH, (Wal lach a West, B 9, 262) Minute needles

Di-methyl-oxamide $C_2O_2(NHMe)_2$. Cone HNO. (Mylius, B 17, 291) Needles yields C₂O₂(NMe NO₂)₂ [124°] (Franchimont, R T C 2, 94, 4, 193) PCl, yields C₄H₅ClN₂

Di-methyl-oxamic acid CO(NMe.) CO.H—CaA'. crystalline (Duvillier, A Ch [5] 23, 315)
Ethyl ether EtA' (c 244°) Not attacked by HNO. (SG 15) (Franchimont a Klobbie, R T C 8, 304)

Ethyl-oxamic acid CO(NHEt) CO.H [120°] Tables — CaA'₂2aq Prisms (Heintz, A. 127, 48) — CaA'₂4aq S 8 17 at 17 5° — BaA'₂ aq

Ethyl ether EtA' (245°) Oil (Wallach, A 184, 59) Decomposed by water

Ethyl-oxamide CO(NH₂) CO(NHEt) [208°] Needles (W)

s-Di-ethyl oxamide CO(NHEt) CO(NHEt) [179°] (Schiff, B 17, 1084) Formed from oxalic ether and ethylamine (W

u-Di-ethyl-oxamide CO(NH₂) CO(NE₁₂) [126°] (268° cor) From CO,Et CO(NEt,) and ammonia (Wallach, A 214, 263) With PCl, it yields 'chloroxalethyline' O,H,ClN, Tri-ethyl-oxamide CO(NHEt) CO(NEt,).

(258°). Formed from diethyl oxamic ether and

ethylamine (W.).

Methyl ethyl-oxamide

CO(NHMe) CO(NHEt) [157°] Formed from methylamine and CO,Et CONHEt (W)
Di 9thyl oxamic acid CO(NEt,) CO,H [101°]

Prisms PCl, yields CO(NEt2) COCl — CaA', 2aq

Ethyl ether EtA' (250°-254°)
Isopropyl oxamic acid CO(NHPr) CO₂H —

CaA'₂ (Duvillier)
Di propyl oxamide Di propyl oxamide C₂O₂(NHPr)₂. [162] Plates, which feel fatty (Wallach, A 214, 312)

Di-isobutyl oxamide [167°] Plates, v sol. alcohol (Malbot, C R 104, 228)

Isoamyl-oxamide [181°]] Di isoamyl-oxamide [129°] Needles

Di amyl-oxamide C₂O₂(NH CH₂CMe₃)₂. [165°]

Needles (Freund, B 23, 2868)

Di allyl oxamide C₂O₂(NHC₂H₅)₂. [154°] (274°) Br yields C₂O₂(NHC₂H₃Br₂)₂ (Wallach a

Strecker, B 13, 513

Ethylene oxamide $C_2O_2N_2H_2(C_2H_4)$ phous precipitate formed, together with soluble (CO₂Et CO)₂N₂H₂C₂H₄ by the action of alcoholic ethylene diamine on oxalic ether (Hofmann, B5, 247) Similar products are obtained from propylene-diamine (Strache, B 21, 2360)

Ethylidene oxamide $C_2O_2N_2H_2(CHMe)$ Formed from cyanogen and crude aldehyde (Ber-

thelot, A 128, 338)

Phenyl examic acid CO(NHPh) CO.H. Oxantic acid [151°] Formed by heating dehy drated oxalic acid (20 g) with aniline (25 g) at 140° for an hour (Laurent, A 68, 15, Claus, Z [2] 4, 158, Aschan, B 23, 1820) The product is crystallised from water and the acid set free by dilute H₂SO₄ Needles (containing Aq) or anhydrous scales (from ether), sl sol cold water, v sol alcohol Yields CO, water, CO, and diphenyl oxamide on heating strongly Yields on nitration p nitro phenyl oxamic scid [210°] crystallising in prisms containing aq (Aschan, The isomeric o nitro phenyl-B 18, 2936) oxamic acid [112°] is formed by heating oxalic acid with o-nitro aniline (Hübner a Heoff, A 209, 367) m Nitro phenyl oxamic ether [150°] is formed from exalic ether and m nitro aniline — NH,A' — (NH,)HA'₂ — KA'aq — NaA'3aq plates, v. sl sol cold water — PbA'₂.—CuA'₂ (Anschütz, B 22, 736) —BaA'₂—AgA' white tables — (NH₂Ph)HA', needles (Chlorade CO(NHPh) COCl needles (from water)

[82°] Methyl ether MeA' [114°] from Me₂C₂O₄ and aniline (Anschutz, A 254, 10)

Plates (from alcohol) or needles (from ligroin) Eithyl ether Eth' [67°] Converted by AcCl into CO(NPhAc) CO.Et [67°] PCl, yields NHPh CCl, CO.Et [72°], which splits up on melting into HCl and NPh CCl CO, Et [91°], whence annine forms NHC, H, CO C(NPh)(NHPh) [235°].

Isopropyl ether PrA' [92°] N Isopropyl ether PrA' [52°] Isobutyl ether C.H.A'. [85°] Amyl ether C.H.A'. Needles Needles. Plates [50°] Needles References -Brown-, CARBOXY, DI-CHLORO-,

and Iodo- PHENYL OXAMIC ACID

Phenyl-oxamide CO(NHPh) CONH. A product of the action of HClAq on cyananiline (Hofmann, A 78, 181) Formed also from phenyl examic ether and NH_a (Klinger, A 184, Crystals (from water)

Di-phenyl-oxamide CO(NHPh) CO(NHPh) Oxamilide [245°] (H), [241°] (T); [252 5°]

(Reissert, B 28, 2245) (320°) Formed by heating annine oxalate at 170° (Gerhardt, A Ch [3] 14, 120, 15, 88) and by decomposing cyananiline with HClAq (Hofmann, A 65, 56, 73, 181, 74, 35) Formed also from ethyl camphor-exalate and aniline (Tingle, C J 57, 655) Nacreous scales, insol water, sl sol hot alcohol

Reactions -1 Nitrous acid passed into its solution in glacial acetic acid forms the nitrosamine CO(NHPh) CO(NPhNO) [86°] and di-pnitro oxanilide (Fischer, B 10, 960, Senf, J prntro examilde (Fischer, B 10, 960, Senf, J pr [2] 35, 521)—2 Chlorine forms tetra chloro diphenyl-examide [c 255°] (Dyer a Mixter, Am 8, 349)—3 Bromine yields C₂O₂(NHC₆H₄Br), [above 300°] whence HNO, yields the nitro-compounds C₂O₂(NH.O₆H₂Br(NO₂)), [288°] and C₂O₄(NHC₆H₄Br(NO₂)), [c 287°] (Mixter a Willcox, Am 9, 362)—4 Iodine HNO, and HOAe yield C₂O₂(NHC₆H₄I[1 4]), 5 Nitric acid forms the compounds (O (NHC H (NO))) (260°) the compounds $C_{0,2}(\text{NH C}_{0}, H_{1}(\text{NO}_{2}))_{2}$ [260°], $C_{1,0}(\text{NH C}_{1}, H_{1}(\text{NO}_{2}))_{2}$ melting at [300°], and $C_{2,0}(\text{NH C}_{0}, H_{1}(\text{NO}_{2}))_{3}$ [300°] (Mixter a Walther, Am = 9, 355, cf Hubner, A = 209, 366) The hexa nitro examilide is converted by aqueous KHCO, into CO(NH2) CO NH C6H2(NO2), [c 260°] and pierie acid Di o and di-m nicro examilides melt above 300° and 270° respectively (H) Di o nitro oxanilide yields, on reduction by tin and HOAc, a base C₁, H₁₀N₄ [above 300°] which forms the salts B"H,Cl, 2aq and B"H,SO, 2aq

References - DI BROMO and TETRA-CHLORO-

PHENYL OXAMIDE

Phenyl oxamide carboxylic acid CO(NH₂) CO NHC₆H₄ CO₂H Formed by boiling the so-called carboxamido carbimidamido benz ore acid CO(NH2) C(NH) NH C6H4 CO2H with water (Griess, B 18, 2411) Small white plates.
—BaA'₂5aq —AgA'

Di-phenyl-oxamide m-carboxylic acid CO(NHPh) CO NHC₆H₄ CO₂H₁ [1 3] benzamic acid [300°-305°] Fo Antloxal-Formed from carboxy phenyl oxamic acid (or its mono ethyl ether) and boiling amiline (Schiff, A 232, 135) Plates (from alcohol)

Anilede NHPh CO CO NH.C.H. CO NHPh.

[290°-295°] Small needles

Di-phenyl-oxamide di m-carboxylic acid C.O. (NH C.H. CO.H.)... Formed by heatin CO.Et CO NH C.H. CO.H (Schiff, A 232, 137) Mono amide C.H. (N.O. (NH.) Forme Formed by heating

Formed by heating amido-benzamide with the compound CO.H. CO.H. CO.H. Crystalline At 200° it yields the imide CieHieN2O4(NH), a powder, insol ammonia

D: amide C2O2(NH C6H4 CO NH2)2 Formed by heating CO₂Et CO NH C₂H₄ CO NH₅ with amido-benzamide Insoluble powder

Di-methyl-amido-phenyl-oxamic

m Amido-phenyl-oxamic acid C.H.(NH2) NH CO CO2H Formed from m-phenylene-diamine and oxalic acid (Klusemann, B 7, 1263) Needles -AgA'

acid

p 278.

anhydrides of the methylo-The hydroxides C.H. NMe. O CO are formed by the action of MeI in MeOH upon the sodium amido-phenyl oxamates, the products being decomposed by Ag₂CO₂ (Griess, B 18, 2408) The secompound crystallises with 8½ aq and yields the salts B'HI aq and B',H,PtCl, The p isomeride crystallises (with 2 aq) in needles, v sol hot water

m-Phenylene-oxamide C2O2(NH)2C6H Formed from m-phenylene-diamine and oxalic ether (K) Amorphous

Di-phényl-di-ethyl oxamide

 $C_{2}O_{2}(NHC_{2}H_{4}Ph)_{2}$ [180°] Crystals (Neubert, B 19, 1826)

Di-phenyl-di-methyl oxamide C₂O₂(NMePh)₂ Formed from methyl aniline and oxalic ether

CO(NHC,H,) CO,H o Tolyl-oxamic acid [137°] Formed by fusing KEtC₂O₄ with o toluidine (Mauthner a Suida, M 7, 233, 9, 735)

Needles (containing aq) Yields indole when heated with zinc dust —CaA'₂ —BaA'₂aq —AgA' p Tolyl-oxamic acid [170°] Obtained from its ether CO(NHC,H,)CO₂Et [67°] which is formed by heating oxalic ether with p toluidine

Nitro tolyl-oxamic acid C.H., N.O. 1 e 4 3] C.H., Me(NO.) NH CO CO.H. Formed by $[1 4 3] C_6 H_3 Me(NO_2) NH CO CO_2 H$ heating nitro-m toluidine with oxalic acid (Hinsberg, B 15, 2691) Yellowish red plates (containing aq) —NaA'aq —BaA', 3aq
Ethyl ether EtA' [127°]

o Tolyl examide CO(NH2) CO(NHC,H,) (Bladin, Bl [2] 41, 129)

D1-o-tolyl oxamide C2O2(NHC2H2)2 Formed by heating oxalic acid with o-toluidine at 220° (M a S) Crystals (from benzene) Converted by treatment with fuming HNO_3 into $\mathrm{C}_2\mathrm{O}_2(\mathrm{NH}\ \mathrm{C}_s\mathrm{H}_2\mathrm{Me}(\mathrm{NO}_2)_2\,[2\ 1\ 3\ 5])_2$ which decomposes at about 270° (Mixter a Kleeberg, $Am\ 11$, 236) On oxidation by neutral KMnO, it yields C₂O₂(NH C₆H₄ CO₂H)₂, which forms the salts Cu₂A"O and Ag₂A".

p-Tolyl-oxamide [237°] Formed CO(NH2) CO(NHC,H,) [237°] Formed from p toluidine cyanide (C,H,NH₂)Cy₂ and HOAc (Bladin) Needles, v sol alcohol

Di-p-tolyl-examide C₂O₂(NHC,H₇)₂ [269°] Crystals, v sol hot HOAc Yields on nitration C2O2(NHC,H6NO2)2 and C2O2(NHC,H5(NO2)2)2

Amido-tolyl-oxamic ether C11H14N2Os 2e C,H,Me(NH2) NH CO CO2Et Tolylene oxam-[168°] Formed from tolylene m diamine and oxalic ether in alcohol (Tiemann, B 8, 222) Plates (from alcohol) When dilute alcohol of 90 pc only is used the acid C₂H₃Me(NH₂) NH CO CO₂H [224°] 18 formed (Schiff, B 23, 1819) Phenyl thiocarbimide yıelds C₆H₃Me(NH CS NHPh) NH CO CO₂Et [155°], a crystalline compound [138°], and $C_eH_2Me < NHC_2O_2 > NPh$ [198°] ClCO.Et [1 2 4] C.H.Me(NH CO.Et) NH C.O.Et forms [181°], whence alcoholic ammonia yields C₄H₄Me(NH CO₂Et) NH C₂O₂ NH₂ [209°] (Schiff a Vanni, B 24, 687, 1315) The compounds 11 4 2] C₄H₄Me(NH CO₂Et) NH C₂O₄Et [128°] and [14 4 2] C₄H₄Me(NH CO₂Et) NH C₂O₄NH₂ [223°] are also crystalline The following bodies of like character are also crystalline: crystalline: or like character are also crystaline: [1 2 4] C₆H₂Me(NH CO NH₂)(NH C₂O₂Et) [218°], [1 2 4] C₈H₂Me(NH CO NH₂)(NH C₂O₂NH₂)[239°], [1 2 4] C₈H₂Me(NH C₂O₂Et) [180°], and [1 2 4] C₈H₂Me(NH C₂O₂Et), [180°], and [1 2 4] C₈H₂Me(NH C₂O₂NH₂), [220°] The compounds [1.2.4] C₈H₂Me(NH CO₂Et) NH C₂O₂II [170°] and

[1 2 4] C_sH₂Me(NH CONH₂) NH C₂O_sH [203°]

have also been prepared.

Amade O.H.Me(NH.) NH C.O.H [1 [223°] From the ether and alcoholus NV.

Antlede C.H.Me(NH.) NH C.O.NPhH[1860]

(Schiff, B 24, 871)

Xylyl-oxamic acid CO(NHC₈H₉Me₂) CO₁H [129°] Formed by heating m xylidine with KEtC₂O₄ (Mauthner a Suida, M 9, 745) Needles (containing aq) On heating it yields di xylyloxamide C2O2(NHC6H2Me2); [210°] -CuA'2--AgA'

ψ-Cumyl-oxamic acid CO(NHC,H,Me,) CO,H [167°] Yellow needles which on heating yield dı ψ-cumyl oxamıde C₂O₂(NHC₆H₂Me₃)₂ [230°] — NaA'Saq -KHA'2 -CaA'2 aq -AgHA'2 -AgA' Di-propyl-di-benzyl-oxamide

C₂O₂(NH CH₂C₆H₄Pr)₂. [182°] (Goldschmidt a Gessner, B 22, 932) Crystalline

Tetra-phenyl di-propyl oxamide

C₂O₂(NH CH₂ CHPh CH₂Ph)₂ [116°] from CH2Ph CHPh CH2NH2 and oxalic ether (Freund a Remse, B 23, 2862) (α) Naphthyl-oxamic acid

CO(NHC₁₀H₇) CO₂H [180°] Formed from oxalic ether and (a) naphthylamine (Ballo, B 6, Needles KA' — CaA'₂ — BaA' — H,NH₂)HA' [154°] Needles (from water)

Ethylether EtA' [106°] Needles

Di-(a)-naphthyl-oxamide C₂O₂(NHC₁₀H₁), 247)(C₁₀H,NH₂)HA'

Dı-(α)-naphthyl-oxamide [200°] Small scales (Zinin, A 108, 228)

C.H. CH(NH) CO. Benzylidene-oxamide Formed from oxamic ether and benzoic aldehyde edicus, A 157, 50) Plates (containing laq)
Piperidyl oxamic ether C₅H₁₀N CO CO₂I t (Medicus, A 157, 50)

(290°) Formed from piperidine and oxalic ether (Wallach a Lehmann, A 237, 245)

Oxamidine $C(NH)(NH_2)C(NH)NH_3$ hydrochloride of this base B'HCl aq is formed by the action of alcoholic NH, on the hydrochloride of oximido ethyl ether (Pinner, B 16, It crystallises in plates, v sol water

Oxalamidoxim C(NOH)(NH₂) C(NOH)(NH₂) [200°] Formed by the action of hydroxylamine on cyananiline or on cyanogen (E Fischer, B 22, 1932, Ephraim, B 22, 2305, Zinkeisen, B 22, 2946, Vorlander, B 24, 814) Colourless prisms, v sol hot water, sl sol alcohol ClCO₂Et forms C(NO CO2Et)NH2 C(NO CO2Et)NH2[168°] Aldehyde produces $CH_{CH} \stackrel{HN}{<} C \stackrel{NH}{<} CHCH_{3}$ [198°] Succinic anhydride yields the acid $CO_2H C_2H_4 C < 0 > N > C C < N > C C_2H_4 CO_3H$ [200°] Chloral yields C₈H₆N₄O₄Cl₈ [197°] — B'HCl prisms, insol alcohol

Di-acetyl derivative [184°] On heating with Ac₂O it yields

 $CM_{\bullet} \leqslant_{O}^{N} > CC \leqslant_{N}^{N} > CM_{\bullet}$ [165°]

D1-bensoyl derivative [217°] Excess of B2Cl forms $PhC \leqslant_{O\ N}^{N} \geqslant C\ O \leqslant_{N\ O}^{N} \geqslant CPh$ [246°], insol water

Di-ethyl ether

C(NOEt)(NH₂) C(NOEt)(NH₂) [115°] Formed from oxalamidoxim, EtI, and NaOEt (Zinkeisen, B 22, 2950) Needles, si sol hot water

Oxaluramidoxim C(NOH)(NH CO NH2) C(NOH) NH CO NH2 [192°]. Formed from oxalamidoxim and conc.

aqueous potassium cyanate (Z) White needles, insol cold water

Phenyl-oxalamidoxim

[c 180°] (Z), [148°] (Fiemann, B 22, 1936) C(NOH)(NHPh) C(NOH)(NH₂) Formed from al oholic hydroxylamine hydrochloride and solid cyananiline (Zinckeisen, B 22, 2954)

 Δ_{C_2O} produces C(NOH)(NHPh) C < N O > CMe

[172°] -B'HCl colourless needles

Di benzoyl derivative [189°] Needles Hydroxylamide of oxalic acid C,O,(NH OH), Formed from oxalic ether and hydroxylamine (Lossen, A 150, 314) Minute prisms (from water) Explodes at 105°—NaHA"—KHA"— CaA'₂ — Ba NH₂(OH)H A" $- \hat{B}aH_{2}A''_{2} - ZnA'' - Ag_{2}A''_{2} -$

Oxalyl-tetra-methyl di hydrazine

Formed from di $C_2O_2(NH NMe_2)_2$ [220°] methyl hydrazine and oxalic ether (Renouf, B 13, 2172) Plates, sol alcohol

Oxalyl-di-ethyl d1-hydrazine

C₂O₂(NH NHEt)₂ [204°] Formed from ethylhydrazine and oxalic ether (Fischer, A 199, 297) Needles Gives rise to the nitrosamine $C_2O_2(N_2HPh\ NO)_2[145^\circ]$, crystallising from water

Oxalphenylhydrazic acid CO(N2H2Ph) CO2H Formed from oxalic ether, phenyl hydrazine, and alcoholic NaOEt (Michael, J pr [2] 35, 459) —NaA' —EtA' [119°]

Oxalyl dı phenyl dı-hydrazıne

 $[278^{\circ}]$ $C_2O_2(N_2H_2Ph)_2$ Formed from oxalic ether and phenyl hydrazine at 110° (E Fischer, Plates With COCl, it yields 190, 131) $C_2O_2(N_2(CO)Ph)_2$ [above 300°]

Semi nitrile of oxalic acid v Cyanoformic

Semi-nitrile of ortho oxalic acid Tri ethyl ether C(OEt)₃CN (161°) S G 155 1 003 Polymenses on standing (Bauer, A 229, 178) Tri propyl derivative C(OPr), CN

(216°-219°)

Nitrile of oxalic acid is Cyanogen

OXALIMIDO ETHYL ETHER C.H., N.O. 2 to C(NH)(OEt) C(NH)(OEt) [c 25°] (c 170°) Formed from cyanogen and alcoholic HCl (Pin ner a Klein, B 11, 1481) Long prisms Benzylamine at 110° forms (CH.PhNH),C₂(NH), [150°] (Vorlander, B 24, 806) p Tolundine forms the isomeric (C₄H₄MeNH),C₂(NH), [220°–230°], which is converted by hydroxylamine sulphate into C(NOH)(NH₄) C(NOH)NHC,H, [175°], which yields a dibenzoyl derivative 194°, and by hydroxylamine hydrochloride into C(NOH)(NH₂) C(NH)NHC,H, [148°], whence may be got C(NOEt)NH₂ C(NH)NHC,H, [133°] and C(NOCH₂Ph)(NH₂) C(NH)NHC H, [165°]

OXALINES A name given to certain alkyl-glyoxalines (Wallach, A 214, 278, 325, Japp, C J 43, 197, Radziszewski, B 15, 2706) They are described as alkyl glyoxalines (v also GLY-

OXAL-METHYL-ETHYLINE v DI-METHYL-

GLYCXALINE OXALMETHYLINE is identical with METHYL-

GLYOXALINE $(q \ v)$ OXAL-METHYL PROPYLINE O METHYL-

ETHYL-GLYOXALINE

OXALOXYL AMIDO-BENZOIC ACID v. CYN-TRIC ACID and CARBOXY-PHENYL OXAMIC ACID.

OXALPROPIONIC ETHER & METHYL OXAL-ACETIC ETHER

OXALPROPYLAMYLINE & PROPYL BUTYL-GLYOXALINE

OXALPROPYLBUTYLINE v DI PROPYL GLY-OXALINE

OXAL PROPYL ETHYLINE v METRYL PRO-PYL GLYOXALINE

OXALPROPYLINE # ETHYL PROPYL GLY-OXALINE

OXALSUCCINIC ETHER

CO₂Et CO CH(CO₂Et) CH₂ CO₂Et (156° at 17 mm) Formed by the action of NaOEt on an ethereal solution of oxalic and succinic ethers (W Wishcenus, B 22, 885) Oil, v sol alkalis FeCl, gives a deep red colour in alcoholic solu-Split up, in dilute solutions, on warming into oxalic and succinic acids and alcohol Yields a phenyl hydrazide

OXALURIC ACID C.H.N.O. 16 L. CO NH CO CO.H. Mol. w 182 NH, CO NH CO CO,H 2,500 (Matignon, C R 113, 198) Occurs as ammonium salt in urine (Schunck, J 1866, 749) Formed by heating parabanic acid with aqueous alkalis (Liebig a Wohler, A 26, 287), and occurs among the products of the action of HCl and KClO, on guanine (Strecker, A 118, 151) Its ether is produced by the action of urea on COCl CO.Et in the cold (Henry, B 4, 644) White crystalline powder, sl soi water It reddens litmus Its aqueous solution is decomposed on boiling into urea and oxalic acid POOL, converts it into parabanic acid (Grimaux, C R 77, 1548) HNO, slowly decomposes it into CO₂ (54 c c), N₂O (38 c c), CO and N (15 c c together) (Franchimont, R T C 6, 216)

Salts -NH,A' silky needles, v sol hot water — KA' aq Trimetric crystals a b c =1 601 539 — CaA', 2aq S 205 at 15°, 5 at 100° (P Waage, A 118, 301) — BaA', 2aq S 158 at 9°, 18 at 100°—AgA' long silky needles

Ethyl ether EtA' [178°] (Salomon, B 9,

374) Silky needles
Amade NH, CO NH CO CO NH, 160°] Formed, together with dialuric acid, by the action of NH, Aq and HCy on alloxan (Rösing a Schischkoff, A 106, 255, Strecker, A 113, 48) Formed also by the action of alcoholic ammonia on oxaluric ether, and of dry NH_a on parabanic acid at 130° (Roudinsköia, Bl [2] 45, 250) Produced by heating ures with oxamic ether (Carstanjen, J pr [2] 9, 143) Crystaline powder, insol cold water Converted into ammonium oxalurate by boiling water

Ozaluryl-hydrasine CO(NH2) CO CO N2H,Ph [215°] Formed by heating phenyl hydrazine parabanate (Skinner a. Ruhemann, C J 53,

550) Dimethyl-oxaluramide O,H,N,O, Formed from di-methyl parabanic acid and alcoholic NH, at 100° (Menschutkin, A 178, 208)

Needles OXALYL-DI CHLORO-ACETIC ETHER v.

Tetra-chlobo tetra-oxy-adipic ether OXALYL - DI - p - DIMETHYLPHENYLENE DIAMINE v Tetra-methyl di amido-di Phenyl-OXAMIDE

OXALYL-METHYL-THIO-URRA v. METHYL THEO-PARABANIC ACID.

OXALYL-METHYL-UREA v Methyl-Para

OXALYL-TOLYLENE-DIAMINE

 $C_0H_1Me < NHCO$ or $C_0H_2Me < NCOH$

Di-oxy-methyl-quinoxaline Formed by heating the acid oxalate of tolylene-diamine to 160° (Hinsberg, B 16, 1531) Converted by PCl_s into C_eH_sMe</br>
N CCl [115°], orystallising in Converted by PCl,

needles, insol water

Oxalyl-di tolylene tetramine

 $C_2O_2(NH O_6H_3Me NH_2[4 1 3])_2$ [above 300°] Formed by reducing di-nitro di tolyl oxamide (v Oxalic acid) Small needles Above 300° it forms $C_eH_sMe < NH > CC NH > C_eH_sMe$

Salts $= B_2H_2SO_45aq - B_2Ol_2aq$ B'H.PtCl

I.PtCl. yellow amorphous pp OXALYL-UREA v PARABANIC ACID

OXAMETHANE is the Ethyl ether of oxamic actd v Oxalic acid

OXAMETHANE CHLORIDE v. DI CHLORO-AMIDO ACETIC ETHER

OXAMIC ACID v Oxalic acid OXAMIDE v OXALIC ACID

OXAMIDINE v OXALIC ACID

ω-OXAMIDO ACETOPHENONE-OXIM

 C_6H_5 C(NOH) CH_2 NH(OH) [163°] Formed by digesting a dilute alcoholic solution of ω bromo-acetophenone with hydroxylamine hydrochloride for several hours at the boiling point White crystalline (Schramm, B 16, 2183) solid Sol alcohol and ether, insol cold water and ligroin Dissolves in alkalis —C.H.N.O.Ag m-OXAMIDO-CARBIMIDO-CARBOXAMIDO-

BENZOIC ACID

(OH)NH C(NH) CO NH CoH, CO2H Formed by the action of an aqueous solution of hydroxyl amine upon cyancarboxamido benzoic acid NC CO NH C₂H, CO₂H (vol 1 p 157) (Griess, B White needles Sl sol hot water -18, 2416) BaA'24aq

OXANILIC ACID is Phenyl oxamic acid v

OXANILIDE 18 Di phenyl oxamide v Oxalio

OXANTHRANOL C,4H,O2 2 6.

-CO- $C_{e}H_{\bullet} < CH(OH) > C_{e}H_{\bullet}$ Anthrahydrogunone Prepared from anthraquinone (1 pt), zinc dust (2 pts), and NaOH (30 pts of 50 per cent solu-tion) The filtrate is ppd by acids, but the ppd oxanthranol must be kept in a closed bottle under carbonic acid water, as it is reoxidised by air to anthraquinone (Graebe a Liebermann, A 160, 126, 212, 65) The red solution of exanthranol in KOHAq is attacked by alkyl iodides forming alkyl-oxanthranols Thealkyl-oxanthranols may be reduced to alkyl anthracene di hydrides, which may be re-oxidised to the alkyl oxanthranols The alkyl oxanthranols give, with PCl_s, alkyloxanthranyl chlorides In these respects methyl oxanthranol behaves differently from the others The alkyl-oxanthranyl chlorides are converted by water back to alkyl-oxanthranols Alkyl-oxanthranols (1 pt) are reduced by zincdust (2 pts) and ammonia (8 pts of SG 88) and water (5 pts) to alkyl hydro anthranols (Liebermann, A 212, 108)

Acetyl derivative C. H.AcO. Formed

from oxanthranol, NaOAc and Ac.O Crystal line solid

Methyl-oxanthranol $C_0H_4 < \frac{CO}{CH(OMe)} > C_0H_{to}$ or C_eH₄ COMe(OH) C_eH₄ [187°] Formed by heating a mixture of anthraquinone, NaOH, zinc dust, wat r, and MeBr (Liebermann a Landshoff, B 14, 456, A 212, 75) Colourless plates, sl sol alcohol, forming a solution with blue fluorescence Reduced by HI and P to anthracene dihydride Not attacked by PCl, An isomeride of methyl oxanthranol [98°] is sometimes formed by the actica of NaOHAq and MeI on exanthranel (Liebermann, B 21, 1175)

Ethyl-oxanthranol C.H. CO CH(OEt) C.H. [107°] Formed from oxanthranol, NaOHAq, and EtI at 100° Formed also by oxidation of CeH4 COEt) CeH4 [77°] with CrO, in HOAc (Goldmann, B 21, 2507) Needles or trimetric prisms, a b c = 741 1 495 Its alcoholic solu tion exhibits strong blue fluorescence It is insol aqueous alkalis Reacts with hydroxyl amine (E von Meyer, J pr [2] 29, 496) HI and P reduce it to ethyl anthracene dihydride Cone H₂SO, forms crystalline C₁₆H₁₂O₂ Yields Yields a di bromo- derivative C₁₄H,Br₂O(OEt) [123°] and a di nitro derivative crystallising in small needles PCl₃ forms C₆H₄ CO CE₄Cl C₆H₄ [89°]

Isobutyl-oxanthranol

 $C_6H_4 < CO_{C(C_4H_9)(OH)} > C_6H_4$ [130°] Prisms or Wolder B 14 462) needles (Liebermann a Walder, B 14, 462) PCl_s yields the chloride C₆H₄ C₂OCl(C₄H₉) C₆H₄ [78°], which reproduces isobutyl exanthranol on boiling with water

Isoamyl-oxanthranol

 C_sH_4 $CO_{(O_3H_{11})(OH)}$ C_6H_4 $(125^o]$ Monoclinic tables (from benzene ligroin) Conc H₂SO₄ removes H₂O, forming $C_{10}H_{10}O$ [72°] which separates from alcohol as yellow needles, and forms a dibromide $C_{10}H_{18}Br_2O$ [120°] ther action of H2SO4 forms a cherry coloured here action of $H_{25}G_{4}$ forms a cherry coordinate in quid, whence alcohol ppts yellow needles of $C_{19}H_{14}O$ [206°], a body which, on oxidation, yields anthraquinone carboxylic acid and a compound $C_{19}H_{12}O_{4}$ [157°] The compound $C_{19}H_{14}O$ is reduced by H in HOAc to $C_{19}H_{18}$ [93°] which crystallises from alcohol in needles, and forms on nitration a compound $C_{19}H_{16}N_2O_5$ (Lieber mann, A 212, 99) Phosphorus pentachloride converts isoamyl exanthranel into the chloride $C_8H_4 < \frac{CO}{CCl(C_8H_{11})} > C_8H_4$ [85°] which crystals, abc=126612752. monoclinic **β** = 68° 23′ NaOAc converts the chloride into C₁₉H₁₉AcO₂ [73°]

Benzyl-oxanthranol $C_{21}H_{10}O_{2}$ [146°] Formed by boiling anthraquinone (5 pts), zinc dust (5 pts), KOH ($7\frac{1}{3}$ pts), benzyl bromide (5 pts), and water (100 pts), for a long time (Levi, B 18, 2153) White tables, v sol alcohol Cone H₂SO₄ at 70° forms a violet solution containing the anhydride C₂₁H₁₄O which crystallises in yellow needles, oxidised by CrO₂ to anthraquin-The anhydride yields a dibromide one.

 $C_eH_i < \frac{CO}{CBr(CHBrPh)} > C_eH_i$ [148°] (Bach, B 23, 1569) which on boiling with alcohol gives $C_{\bullet}H_{\bullet} < \frac{CO}{C(CBrPh)} > C_{\bullet}H_{\bullet} [254^{\circ}]$

Acetyl derivative

 $C_{e}H_{4} < CO \longrightarrow C_{c}(CH_{2}Ph)(OA_{0}) > C_{e}H_{4}$ [281°] Needles (β) Oxanthranol C14H10O2 2 e

C(OH) C,H, Obtained by careful oxi-`Ċ(OH)∕

dation of anthracene by adding 56 grms of lead peroxide to a hot solution of 2 grms of pure anthracene in 50 cc of acetic acid (Schulze, B 18, 3036) Greenish yellow needles (from alcohol) The alkaline solution is red, but quickly becomes decolourised on shaking with air from oxidation to anthraquinone is very oxidisable. In its properties it closely resembles oxanthranol With ammoniacal AgNO, it gives a pp of metallic silver Cupric hydrate mixed with excess of NaOH is reduced to black cuprous oxide

Dr methyl ether C_{1.}H_n(OMe), [196°]
Dr ethyl ether C_{1.}H_n(OEt), crystals
Dr benzyl ether C_{1.}H_n(OC,H), [220°];

small colourless glistening crystals

Di acetyl derivative $C_{^{\rho}}H^{4} < \stackrel{C(\mathrm{OAc})}{C(\mathrm{OAc})} > C_{^{\rho}}H^{4}$ $[260^{\circ}]$ Formed from ordinary oxanthranol, Ac,O, and NaOAc (L)

Needles (from HOAc) D1-0xy-(β)-oxanthranol v TRI OXY ANTHRANOL OXATOLUIC ACID v DI BENZYL GLYCOLLIC

OXAZINES Compounds derived from the hypothetical oxazine NH CH CH CH O Quin-

oxizine is $C_6H_1 < {O CH CH}$

OXAZOLES Compounds derived from the hypothetical oxazole N CH CH O (Hantzsch, B

OXETHYL. v OXY ETHYL

OXETONES Compounds derived from the $CH_2 < CH_2 \longrightarrow CC < CH_2 \longrightarrow CH_2 \longrightarrow CH_2$ hypothetical

They are formed by treating lactones with sodium and heating the products (Fittig, A 256, 57) Thus valerolactone C.H.S.O. yields C. H.J.O., which, when boiled with NaOHAq forms C. H.B.NaO., which is split up by heat into CO, and di methyl oxetone

 $CH_2 < \begin{array}{c} CH_2 \\ CHMe \end{array} > C < \begin{array}{c} CH_2 \\ O \end{array} > CH_2 \\ > CH_2$

This term was used formerly to connote chemical changes wherein oxygen was added on to an element or compound, or a compound was decomposed by the action of O with formation of oxidised products The term was nearly synonymous with combustion in the earlier and more restricted meaning of that word For an account of the phlogistic theory of com bustion v Combustion, vol 11 p 241

The term oxidation has been widened until at present it is applied to all chemical changes which result in an addition of negative radicle. simple or compound, to elements or compounds, or a decrease in the relative quantity of the positive radicle of a compound, whether this is or is not accompanied by substitution of negative radicle. Thus the following changes negative radicle Thus the following are classed together as oxidations $-4Fe+3O_1$ $^{OE}-O$ $^{OE}-A$ $^$ = $2 \text{Fe } O_3$, $2 \text{Fe } + 3 \text{Cl} = 2 \text{Fe } O_3$, $2 \text{Fe } + 3 \text{Cl} = 2 \text{Fe } O_3$, $2 \text{Fe } + 3 \text{Cl} = 2 \text{Fe } O_3$, $2 \text{Heg } + \text{L}_2 = 2 \text{Hg } I_2$, $2 \text{KNO}_2 + O_2 = 2 \text{KNO}_3$, $2 \text{Heg } + \text{L}_2 = 2 \text{Hg } I_2$, $2 \text{KNO}_2 + O_2 = 2 \text{KNO}_3$, $2 \text{Fe } O_3 + 2 \text{Hg } O_3 + 2 \text{Hg } O_3$, $2 \text{Fe } O_3 + 2 \text{Hg } O_3 + 2 \text{Hg } O_3$, $2 \text{Fe } O_3 + 2 \text{Hg } O_3 + 2 \text{Hg } O_3$, $2 \text{Fe } O_3 + 2 \text{Hg } O_3 + 2 \text{Hg } O_3$, $2 \text{Fe } O_3 + 2 \text{Hg } O_3 + 2 \text{Hg } O_3$, $2 \text{Fe } O_3 + 2 \text{Hg } O_3 + 2 \text{Hg } O_3$, $2 \text{Fe } O_3 + 2 \text{Hg } O_3 + 2 \text{Hg } O_3$, $2 \text{Fe } O_3 + 2 \text{Hg } O_3 + 2 \text{Hg } O_3$, $2 \text{Fe } O_3 + 2 \text{Hg } O_3 + 2 \text{Hg } O_3$, $2 \text{Fe } O_3 + 2 \text{Hg } O_$ $\begin{array}{l} 2K_1FeCy_0 + Cl_2 = 2K_1FeCy_0 + 2KCl, \\ 2Cr.O_1 + 4K_2O + 3O_2 = 4K_1CrO_1, \\ 4K_2MO_1 + 2K_2MO_2, \\ 4K_2MO_1 + 2K_2MO_2, \\ 4K_2MO_1 + 2K_2MO_2, \\ 4K_2MO_1 + 2K_2MO_2, \\ 4K_2MO_2 + 4K_2MO_2, \\ 4K_2$ = B₁₂O₂ + 4KCl + 4HO₂ $3C_2H_0O + 2CrO_1$ $=3C_{2}H_{1}O + 3H_{2}O + Cr_{2}O_{3}$

Processes of oxidation are accompanied by processes of reduction or deoxidation. The following examples make this clear (cf Deoxida Tion, vol 11 p 377) -

Original clement Oxidised Deoxidised or compound Product H, но 0 H_0 (The H₂O may be regarded as oxidised H, or as reduced O 2Hg Hg O (The O₂ may be regarded as reduced ozone [O₃]) SbCL SbCl, SbCI. (The SbCl, is oxidised SbCl, or reduced Cl) SnO₂+HO + 6CO + 3HO + N.O. 2HNO 3H C OAAq $2MnO_2 + K_2OAq$ 2KMnO,Aq (PbO PbO2 + H2O 2Cl + 2KOHAq 2KClAq K_4FeCy_6Aq Cl_2 K,FeCy,Aq 2KClAq 4K,MnO,Aq + (In the three cases in the bracket, KCl and K₂O may be regarded as reduced Cl and O respectively 3H,SO,Aq 3SO Aq $2HNO_{s}Aq + 2H_{s}O =$ 2NO

They are formed by the action of the halogen derivatives of ketones on acetamide and its homologues, eg Ph CO CH.Br + Me CO NH,

$$= PhO < \begin{array}{c} CH O \\ N CMe \end{array} + HBr + H_2O$$

Compounds derived from CH CH N >0 may be

called is oxazoles. Thus phenyl isoxazole is formed by the action of AcCl on the oxim of benzoyl acetic aldehyde (Claisen B 24, 134) Vor. III

Any element or compound which frequently reacts to produce substances containing rela tively more negative radicle than the original substance acted on, is called an oxidiser or oxidising agent Among the substances commonly used in the laboratory to effect oxidations are oxygen, ozone, chlorine, hypochlorites, nitrie acid, potassium permanganate, potassium chlor ate, molten potash, and chromium trioxide The conditions under which oxidation occurs vary much, thus Hg is oxidised by ozone at the 658 OXIDATION.

ordinary temperature, but by O only at tempera tures near the BP of Hg, KMnO,Aq oxidises H,O,Aq completely only in the presence of H2SO4, and at a moderately high temperature, O does not oxidise SO, under ordinary conditions, but if the gases are passed over hot spongy Pt, SO, is produced rapidly When O is absorbed by charcoal, and the charcoal is then brought into contact with H_2S , PH_3 , C_2H_6O , &c, oxidation proceeds rapidly (v. Calvert, C. J. [2] 5, 293) The products of oxidation obtained from a specified substance often vary according to the oxidiser employed, thus ozone produces Hg2O from Hg at ordinary temperatures, but HgO is formed by the action of O on hot Hg, carbohydrates generally give H CO2H when oxidised by CrO3, but H₂C₂O₄ when oxidised by HNO₃, phthalic acids, C₆H₄(CO₂H)₂, are obtained by oxidising naphthalene, C₁₀H₈, by CrO₃ in glacial acetic acid, but the chief product of the oxidation of the same compound by K₂CrO₄ and H₂SO₄Aq (which is essentially a solution of CrO_3) is naphthaquinone, $C_{10}H_6O_2$. There are some compounds the presence of which in a solution of an oxidisable body hastens the oxidation when O is passed into the solution, thus, H2C2O4Aq is oxidised by CrO, Aq in presence of MnSO, (Harcourt, B A 1864 34), SO Aq is rapidly oxidised by O in the presence of certain salts, especially MnSO₄, CuSO₄, FeCl₅, CoCl₂, &c (v L Meyer, B 20, 3058, Roessler, D P J 242, 278, cf Mendelejeff, B 19, 2656) MMPM

OXIDES Binary compounds of oxygen For the purposes of this definition, those compounds of O with organic radicles which react similarly to oxides of elements must be classed among binary compounds (e g the ethers), in the present article, however, only the binary compounds of O with elements are considered Oxides of all elements except Br and F have been

isolated

Oxides are frequently prepared by the direct union of O with other elements, O unites directly with all the elements except Br, Cl, F, I, Au, and Pt Metallic oxides are formed by the action of heat on carbonates, nitrates, and other salts of volatilisable acids, but the alkali oxides cannot be thus prepared Most (?all) metals decompose water or steam, forming oxides or hydroxides, and evolving H Many metallic sulphides yield oxides when roasted in air or O Those oxides or hydroxides of metals which are not easily soluble in water are generally formed by the reaction of alkalis or alkaline oxides with solutions of metallic salts The higher oxides of metals are often obtained by the action of hypochlorites, or Cl and KOHAq, on the lower oxides, sometimes by the action of conc HNO, on the lower oxides or the metals, and sometimes by reacting on salts of the metals in solution with H₂O₂Aq in presence of an alkali

Fusion of metallic oxides with KOH or KNO, generally results in the formation of alkali salts of metal-containing acids in the cases of those metals which are capable of forming such salts. The higher oxides of metals are generally more or less easily reduced to lower oxides, this reduction occurs sometimes by heating, in other cases by the action of such reducers as H, CO, SO₂Aq, or H₂S. The oxides of non-metals are frequently formed by combining O with the non

metal, eg B₂O₃, SO₂, SO₃, CO, CO₂ H O, NO₃, P₂O₃, P₂O₅, sometimes they are produced by such indirect methods as decomposing oxyacids or salts of oxyacids of the non-metals, eg N₂O₄ from HNO₃, I₂O₅ from HIO₃, ClO₂ from KClO₃, sometimes they are formed by very indirect methods, eg Cl₂O by the reaction of Cl with H₂O₄.

Oxides may be divided into classes in accordance with their empirical composition, thus, monoxides, M₂O and MO, sesquioxides, M₂O, dioxides, MO₂, trioxides, MO₃, tetroxides, MO₄,

pentoxides, M₂O₅, heptoxides, M₂O₇

A better classification is that based primarily on chemical properties, on this system, oxides are classified as basic, acidic, indifferent or neu tral, and peroxides None of these terms can be defined with strictness The term basic is applied to those oxides which react with acids or with oxides more negative than themselves to form salts Acidic oxides are those which react with water to produce acids, or are formed by removing water from acids, or react with oxides more positive than themselves to form salts Acidic oxides are sometimes called anhydrides Peroxides react with acids to form salts which correspond with oxides containing less O than the peroxides Some peroxides also form acids when dissolved in water, or react with acidic oxides to produce salts Peroxides which exhibit acidic functions may be called acidic peroxides, eg CrO, peroxides which exhibit no acidic functions may be called basic peroxides. eg BaO, Certain other oxides are sometimes included in the class peroxides (v infra) class of indifferent or neutral oxides includes all oxides not belonging to one or other of the three preceding classes

Most of the lower oxides Basic oxides of metals belong to this class The characteristic reactions of the class are shown by the following two typical changes -BaO+H SO,Aq $= BaSO_4 + H_2OAq$, $PbO + SO_3 = PbSO_4$ None of the oxides of any undoubted non metal is dis tinctly basic Oxides of non metals, however, exist which form salts by reacting with certain strong acids, or the anhydrides of certain strong acids, and which also form salts by reacting with oxides more basic than themselves, thus, $\rm B_2O_3$ reacts with $\rm H_2SO_4$ containing $\rm SO_3$ to form B(HSO₄), and B₂O₅ also reacts with K₂O to form K₂B O₄, similarly As₂O₅ reacting with SO₅ forms compounds belonging to the salt type, xAs₂O₃ ySO₃, and with K₂OAq it forms KAsO₂.

Some metallic oxides are basic, and nevertheless also form compounds with water which react as weak acids towards the more positive oxides, thus Al₂O₂ is distinctly basic, Al₂O₃ H₂O is also basic, yet it reacts with K₂OAq to form the unstable salt K₂Al₂O₄, similarly Au O₄ 3H₂O dissolves in HNO₂Aq to form the salt Au(NO₂), and Au₂O₃ BH₂O also dissolves in K₂OAq to form K₂Au₂O₄. The term basic oxide is sometimes widened to include oxides which correspond with salts, although these salts may not be formed directly from the oxides, thus, no salts have been obtained by the action of oxyacids on OsO, but a few salts corresponding with this oxide are produced by indirect methods, eq. OsSO₂ is formed by reacting on OsO₄Aq with SO₂Aq. The alkals-forming oxides constitute a

OXIDES 659

division of the basic oxides, these oxides are distinctly and markedly basic, they also dissolve in water to form alkalis (v Aleali, vol 1.

p 111, v also Base, vol 1 p 445)

Audic oxides or anhydrides greater number of the oxides of non-metals belong to this class SO, is a typical acidic oxide, it reacts with water to form the acid H₂SO₄, it is obtained by removing H₂O from H2SO4, by heating the acid, it reacts with basic oxides to form salts, eg with BaO it produces BaSO, All acidic oxides do not exhibit the three characteristic reactions, some yield acids with water, but are not obtained by removing water from their acids, eg P₂O₃, some are obtained by removing water from acids, but do not react with water to form acids, eg Sb₂O₃, some do not form acids with water, are not ob tained by removing water from acids, but react with oxides more positive than themselves to produce salts, e g As₂O₈ Those acidic oxides which do not form corresponding acids by reacting with water generally show basic functions when they react with strong acids Should an oxide form no acid with water, nor be obtained by removing water from an acid, but yet react with basic oxides to form salts, this oxide, although classed as acidic, will be found, almost certainly, to react as a basic oxide towards strong acids, or the anhydrides of strong acids Thus, As2O2 does not form an acid with water, nor is it obtainable from a corresponding acid, it does, however, react with strongly basic oxides, e g with K2OAq, to form salts, now As2O, combines with SO, to form As,O, 2SO, a compound in which As,O, acts as a basic oxide Some of the higher oxides of metals react as feebly acidic oxides, the salts corresponding with these oxides are generally obtained by fusing the oxides with KOH or NaOH (v Anhydrides, vol 1 p 267)

that correspond with oxides containing less O than the peroxides The following reactions exhibit this typical property of peloxides – $BaO_2 + H_2SO_1Aq = BaSO_4 + H_2OAq + O$, $2CrO_3 + 12HClAq = 2CrCl_3Aq + 6H_2O + 3Cl_2$ Some oxides which react in this way also ın water to form acids, $CrO_3 + H_2O + Aq = H_2CrO_4Aq$, others do not form acids with water, but react with strongly basic oxides to produce salts, eg PbO₂+K₂O (molten) - K,PbO, Peroxides which exhibit acidic functions may be called acidic peroxides, e g CrO₃, PbO₂, peroxides which do not exhibit acidic functions, ie which do not form acids with water, nor salts by reacting with basic oxides, may be called basic peroxides, e.g. CaO2, K₂O₄ The more important oasic percentage Na₂O₅, K₂O₄, CaO₂, SrO₂, BaO₂ (?)CdO₂, CuO₂, (?)D₂O₅ Among the acidic percentage may be mentioned CrO₅, PbO₂, and MnO₂. Several networks of metals cannot be assigned with certainty to the class of acidic peroxides, or to that of basic peroxides; eg Bi₂O₈ reacts with acids as a basic peroxide, and probably forms salts by fusion with a large excess of KOH, but the salts have not been isolated, UO, is distinctly scidic, with soids it forms uranyl salts,

oxides which react with acids to produce salts

Peroxides

This class includes those

action of acids, but these reactions have not been examined sufficiently

The term peroxide is used sometimes to include any oxide of a specified element which contains more O than the highest definitely basic or acidic oxide of that element This statement does not define peroxide, because no formal definitions of the terms definitely basic oxide' and 'definitely acidic oxide' can be given Such oxides as S2O,, Cr2O, (if it exists), MnO2, and Mn2O2, would thus be classed as per-

oxides (v infra)
Indifferent or neutral oxides Oxides which do not form acids with water, are not ob tained by removing water from acids, and do not form salts by reacting with either basic or acidic oxides, or with acids, are generally called neutral or indifferent oxides Examples of such oxides are H₂O, NO, P₄O, (?)Fe₃O₄, Pb₂O, Ag₄O,

(?)Mn₃O₄

None of the qualifying terms applied to oxides can be defined with strictness, such an oxide as MnO2 is basic, because it forms salts by reacting with acids, MnO2 is also acidic, because when fused with K2O, in presence of O, it forms a salt (K2MnO4), it is also a peroxide, because the salts which it forms with acids correspond with the lower oxide MnO, and lastly, it may be classed as an indifferent oxide, because it does not form an acid with water, is not ob tained by removing water from an acid, and does not form corresponding salts by the action of acids, acidic oxides, or basic oxides it is remembered that the properties expressed by the terms basic oxide, acidic oxide, and peroxide, are properties which come into play only when the oxides react with other substances, it is evident that these properties must depend to some extent on those of the other substances Keeping this in mind, one sees how difficult, if not impossible, it must be to define the properties in question

Oxides have been classified as indifferent and salt forming, and the salt forming oxides have been subdivided into those which form corresponding salts by reacting with acids or negative oxides, those which form corresponding salts by reacting with basic oxides, and those which form salts but not corresponding salts, by one or other of these reactions This classification is practically the same as that which has been sketched already, although it is expressed in somewhat different terms

What is the composition of the basic oxides? Which elements form acidic oxides? Can the composition of peroxides be stated in general terms? Alkalı forming oxides are oxides of the most positive metals The following are usually included in this group —Li₂O, Na₂O, K₂O, Rb₂O, Cs₂O, Tl₂O; MgO, CaO, SrO, BaO, (?Ag₂O, ?PbO) Basic oxides, which are not alkali forming, are oxides of fairly positive metals eg BeO, ZnO, CdO, HgO, Sc_2O_3 , La_2O_3 , Al_2O_3 , Ga_2O_3 , Fe_1O_3 , NiO_3 , CoO_2 , TiO_2 , ZrO_2 , SnO_3 , SnO_2 , PbO_3 , Bi_2O_3 , Acidicoxides are oxides of negative elements, or they are compounds of elements, which on the whole are positive, with relatively much O, eg N₂O₂, N₂O₃, P₂O₃, P₂O₃, Cl₂O, I₂O₃, SiO₂, CO₃, CrO₃, UO₃, Ta₂O₃ Peroxides, in the sense explained eg UO₂ SO₄; OsO₄ is slightly acidic, no corresponding salts have been obtained by the re660 OXIDES

also include some of the highest oxides of nonmetals, eg. 820, Two oxides of the same element may exist, and one of these may be a basic, and the other an acidic, oxide, thus Cr2O2 is basic, but CrO, is acidic Hence, whether an oxide is basic or acidic seems to depend not only on the general chemical character of the element combined with O, but also on the relative quantities of O and the other element None of the elements whose lower oxides are alkaliforming forms an acidic oxide, but some of these elements form basic peroxides, in other words, the association of much O with a very distinctly positive element does not produce an acidic oxide, but does produce a basic peroxide impossible to divide the elements into two classes, and say all on one side of the division line generally form basic oxides, but may also form acidic oxides All that can be said is, the lower oxides of the metallic elements, as a class, are basic, but many of these elements also form higher oxides, some of which are distinctly acidic, and some are acidic peroxides, the oxides of the non metallic elements as a class, are acidic, but some of these elements also form indifferent oxides, and a few oxides of non metals are peroxides

The peroxides have been divided by Men delejeff into two classes (J R 1881, [1] 561, abstract in B 15,242, v also Traube, B 19,1111, 1115,1117, Richarz, B 21,1675) Mendelejeff distinguishes peroxides belonging to the type H₂O from those which belong to the type H₂O, the latter class he calls superoxides, the former polyoxides. In the polyoxides, according to M, the O is all in direct union with the other element, and none of the O atoms is directly united with any other, whereas the O atoms of superoxides are regarded as in direct union with each other, as well as with the other element BaO₂ is a typical superoxide, and is

supposed to have the structure Ba

is a typical polyoxide, and is supposed to have the structure O Mn O. The views of Traube (lc) and Richarz (lc) are practically the same as those expressed by Mendelejeff. The superoxides yield H₂O₂Aq by reacting with dilute acids, and therefore reduce KMnO₄Aq in presence of H₂SO₄, the polyoxides do not yield H₂O₂ but H₂O and O. Peroxides formed by the action of alkaline oxidisers, eg. KClOAq, seem always to belong to the class of polyoxides. The peroxides K₂O₄, Na₂O₅, CaO₂, SrO₂, BaO₂, ZnO₂, CdO₂, CuO₂, Di₂O₄, and some others, are superoxides, ie they give H₂O₂Aq when acted on by dilute acids. According to Mendelejeff, S₂O₇ is a superoxide, it gives H₂O₅, when dissolved in much water, the constitution is probably O.SO₂.

Mendelejeff (Ic) says that the power possessed by any element of forming a characteristic basic or acidic oxide, from which salts are obtained, is connected with the position of the element in the periodic scheme of classification But besides forming a salt-forming oxide, or more than one such oxide, some elements are also capable of producing superoxides belonging

o so

to the type HO OH. Glancing at the groups of elements, as the elements are arranged in the periodic scheme of classification (v. Classification, vol ii p 204), and expressing the composition of the highest characteristic oxides of each group in a general formula, we have the result shown in the table on p 661

The molecular weights of very few oxides have been determined with certainty, on this subject v Henry, P M [5] 20, 81, cf Carnelley a Walker, C J 58, 59 M M P M

OXIDO-DI-NAPHTHYL-AMINE v. IMDO-DI-NAPHTHYL OXIDE

OXIMIDO ACETIC ETHER 7,H,NO, t.e. OH(NOH) CO,Et Netroso-acetic ether Formed, together with oxalio acid, by the action of fuming HNO, on aceto acetic ether (Pröpper, A 222, 48) Oil Yields oxalic acid and hydroxylamine when heated with HClAq at 140° Cold KOHAq yields KCy, K,CO,, and alcohol.—(NH,)C,H,NO, aq silky needles —C,H,NaNO, aq needles (from wester)

OXIMIDO-ACETOACETIC ETHER v NITEOSO-ACETOACETIC ETHER

OXIMIDO- compounds v. Nrrsoso- com pounds

OXIMIDO - ETHER v OXALIMIDO - ETHYL ETHER

TRI-OXIMIDO-METHYLENE C₂H₂N₃O₂ * e CH₂\(\times\)N(OH) CH₂\(\times\)N(OH) Formed from formus aldehyde and hydroxylamine (Scholl, B 24, 574) White amorphous solid, insol water, alcohol, and ether At 133° it passes directly into a

OXIMIDO-NAPHTHOL v AMIDO NAPHTHO-

OXIMS or OXIMES Compounds containing the group CNOH, obtained by the action of hydroxylamine on aldehydes, ketones, and ketonic compounds, by the reaction RR'CO + H.N OH ERRC(NOH) + H₂O (V Meyer, B 15, 1164, 1324, 1525, 2784, 16, 822, 2992, 19, 1613) (v Aldonims, vol 1 p 111) The reaction is best Aldoxims, vol 1 p 111) performed with hydroxylamine hydrochloride (1 mol) and aqueous NaOH (3 mols) in the cold (Auwers, B 22, 604) Oxims are split up by boiling HClAq into hydroxylamine and the original aldehyde or ketonic compound The oxims do not exhibit Liebermann's reaction with phenol and H₂SO₄. The oxims yield acetyl, alkyl, and sodium derivatives. Ketoxims (1 e oxims of ketones) are converted by warming with cone H₂SO₄ at 100° into the isomeric amides, thus Ph₂C NOH becomes Ph CO NHPh, while PhMeC NOH yields acetanilide (Beckmann, B 20, 1507, Wegerhoff, A 252, 1, Gunther, A PCl, acts like H2SO4 Oxims are 252, 44) readily reduced, in alcoholic solution by means of sodium amalgam and acetic acid, to the corresponding amines, thus XYC NOH + 2H, = XYCH $NH_2 + H_2O$ (Goldschmidt, B 19, 3232) Benzoic aldehyde gives two oxims and two sets of alkyl oxims (Beckmann, B 22, 1534), and benzil also gives a greater number of oxims and alkyl-oxims than the ordinary formulæ indicate These isomerisms may perhaps be explained by considering the arrangement in space of the atoms in the molecule (Beckmann, 20, 2766, B 23, 1680, Auwers a V Meyer, B 21, 784, 22, 1996, 28, 2408, Hantzsch, B 24, 31, 1192).

Groups	•	I.			II.		III
Elements in group Composition of highest basic or acidic counteristic of the group Character of highest basic or acidic oxide characteristic of the		H, L ₁ , Na, I Ag, Cs, Au	K, Cu, Rb,	Be, Mg, Ba, Hg	Ca, Zn, Sr, C	d, B,	Al, Sc, Ga, Y, In, a, Yb, Tl
		M,O		мо			M₃O₀
group		Bas	10		Basic		nich is a weak an
Superoxides, ty HO OH	pe of	H ₂ O ₂ , Na ₂ O ₂ , Ag ₂ O ₂	K ₂ O ₄ , CuO ₂ ,	CaO ₂ , Zr BaO ₂	1O ₂ , SrO ₂ , CdC		(? TlO ₃)
Groups		IV	v		٧ı		AII
Elemen ts in group		Tı, Ge, Zr, Ce, Pb, Th	N, P, V, Sb, D1, L:		(O), S, Cr, S Te, W, U	e, Mo,	F, Cl, Mn, Br, I (group very moomplete)
Composition of highest basic or acidic oxide characteristic of the group		MO ₂	M₂C),	МО₃		M ₂ O ₇ , represented only by Mn ₂ O ₇ [Cl ₂ O, ClO ₂ , I ₂ O ₃ , no oxide of F or Br]
Character of highest basic oracidic oxide characteristic of the group	or Si basic Ge, 2 Pb more incre	when M = C a, acidic and when M = Ti, Zr, Sn (? Ce), (becoming basic as M cases), basic a M = Th		ets as a	Acidic, becless acidic increases, shows som properties	as M UO,	Aoidi e
Superoxides, type of HO OH	Tı	O _s , CeO _s	(? NO ₃ , ?	D1 O5)	S ₂ O ₇ (? Cr ₂ O ₇ ,	(OU:	none

Group VIII

;	Family 1 Fe, Ni, Co	Family 2 Ru, Rh, Pd.	Family 8 Os, Ir, Pt.
Highest characteristic oxide	M O ₃	MO ₄ , represented only by RuO ₄	MO ₄ , represented only by OsO ₄
Character of oxide	Basio	Feebly acidic (These elements also form MO, M ₂ O ₃ , and MO ₂ , which are feebly basic)	Feebly acidic (These elements also form MO, M ₂ O ₂ , and MO ₂ , which are feebly basic)
Superoxides, type of HOOH	? FeO ₂ , ? N ₁ O ₃ xO, ? Co ₂ O ₃ xO	none	none

Oxims of ketones may be changed to phenylhydrazides by heating with phenyl hydrazine (Just, B 19, 1205)

OXINDOLE C, H, NO t.c. C, H, < CH2 > CO or

C.H. CH₂ COH (Baeyer a Comstock, B 16, 1704) Anhydride of o-amido-phenyl acetic acid Mol w 188 [120°] Formed by reducing o-intro-phenyl-acetic acid with tin and HCl Obtained also by reducing dioxindole with sodium amalgam (Knop, J pr 97, 65, Baeyer a Knop, A 140, 1, Baeyer, B 11, 588, 12, 457) If the mixture of isomeric nitro-acids got by heating phenyl-acetic acid with fuming HNO, on the water bath be reduced with tin and HClAq, and, after removal of tin by H₂S, be boiled with

BaCO₃, only the *m*- and *p*-nitro phenyl acetic acids will form barium salts, and the oxindole may be extracted by ether

Properties — Long colourless needles (from water) Oxidised slowly by moist air, forming dioxindole Reduces ammoniacal silver nitrate, forming a mirror Extracted by ether from its alkaline solution Not affected by boiling baryta water, but at 150° it yields barium amido phenylacetate Nitrous acid forms nitroso-oxindole which is an oxim of Isatin PCl, yields Cc.H. CHCl COL [104°] reduced by iron-filings and KOH to indole

Salts —AgC,H,NO —B'HCl. deliquescent spicules

Acetyl derevative [126°]. Long colour-

OXINDOLE. *8*69

less needles SI sol cold water and ligroin, v sol alcohol (Suida, B 12, 1326) Converted by dilute NaOHAq into O.H. (NHAc) CH. CO.H. [142°

Brome-oxindole C.H.BrNO [176°] Formed, together with tri bromo-oxindole C,H,Br,NO 2aq, by the action of bromine water on oxindole Both compounds form feathery crystals

Nitro-oxindole C.H. (NO2)NO Prepared by nitration Yellow needles, sol alcohol Begins to decompose at 175°.

Amido-oxindole $\begin{bmatrix} 4 & 1 \\ 2 \end{bmatrix}$ $C_6H_3(NH_2) < \begin{pmatrix} OH_2 \\ NH \end{pmatrix} > CO$ [c 200°] Prepared by reduction of (4,2,1)-dinitro phenyl acetic acid (Gabriel a Meyer, B 14, Long spikes, v sol hot water

Exo-amido-oxindole $C_0H_1 < \frac{CH(NH_2)}{NH} > CO$

The hydrochloride, formed by reducing isatin-oxim with tin and HClAq, is decomposed by water, yielding a red resin

Methyl-oxindole v p 351

Ethyl-oxindole C₆H₄ CH₂ CO Formed by heating oxindole with EtI and NaOEt al sol water Very difficult to saponify by acids or alkalıs

Dioxindole C₆H NO₂ v.e C₆H₄ $< \frac{\text{CH(OH)}}{\text{NH}} > \text{CO}$

Isatın dihydride Anhydride of Hydrindic acid Mol w 149 [180°] S 85 in the cold, 17 at 100° S (alcohol) 7 in the cold, 10 at 78° Formed by reducing an aqueous solution of isatin with zinc dust and HClAq, and extracting with ether (Baeyer, B 12, 1309) Yellowish monoclinic prisms (from water) or colourless crystals (from alcohol) Forms a violet liquid on melting Its aqueous solution becomes red on exposure to the air, forming isatyde and isatin In acid solution it may be reduced to oxindole Chlorine forms chloro dioxindole C₈H₆ClNO₂ and dichloro-dioxindole C₈H₅Cl₂NO₂ The corresponding bromo-derivatives melt at 165° and 170° respectively PCl₅ yields C₈H₅Cl₂N Ammonia colours its solution violet, and on boiling throws down a violet colouring matter, sol HClAq Potash and baryta produce a dark-violet colour, changing to red and finally yellow

Salts - C.H., NO2HCl nodular crusts -C.H.NO.H.SO. aq ppd by adding water to its solution in H.SO. —NaC. H.NO. 2aq silvery scales, v sol water, insol alcohol —BaA. 24aq white cubes, sl sol water Gives off aniline on heating —PbA'₂ 2aq ppd by lead subacetate AgA' crystalline pp Gives off benzoic ald Gives off benzoic alde-

hyde at 60°

Acetyl derivative C,H,AcNO, Short prisms, sl sol cold water (Suida, B 12, Cold baryta water converts it into acetylacid C₆H₄(NHAc) CH(OH) CO₂H hydrindic [142°] which is also formed by reducing acetylisatic acid with 3 pc sodium amalgam in acid solution (Suida, B 11, 586)

Witroso-dioxindole C.H.(NO)NO2 810°] Formed by passing nitrous acid vapour into an alcoholic solution of dioxinacie Yellowish erystals, sl. sol water May be sublimed On boiling with FeSO, and KOHAq it yields 'azodioxindole' C.H.N.O. which is ppd by HOlAq in white needles [300°], yielding with AgNO, and NH, a white pp of Ag.C.H.N.O. Sodium-amalgam

and a little water reduce nitroso dioxindole to 'azoxındole' C₈H₆N₂O, ppd by HClAq as an amorphous powder (containing saq) and crystallising from alcohol in cubes Bromine water converts nitroso dioxindole into C.H.Br.N.O. 3a(1

Salts —NH₄C₅H₅(NO)NO₂ 1½aq white silky laminæ —BaC₅H₄N₂O₂ —AgC₅H₅N₂O₃ yellowish-

OXOCTENOL C.H. O. 1.6.

 $CMe_3 C(OH) < OMe_2 ? [49 5°] (178°).$ 48 (at 185°) A product of the oxidation of isodibutylene by KMnO, (Butleroff, J R 14, 203, C J 42, 936, Bl [2] 38, 553) Long thin prisms, smelling like camphor, sl sol water, v sol alcohol and ether Does not react with hydroxylamine (Meyer a Nageli, B 16, 1622) Not attacked by hot bromine

Acetyl derivative C.H. AcO2

Formed by heating with Ac₂O at 150°

OXOCTYLIC ACID v OXY-OCTOIC ACID OXONIC ACID C4H5N3O4 A salt of this acid is formed by the atmospheric oxidation of an alkaline solution of uric acid (Strecker, Medicus, A 175, 230, B 10, 546) The free acid splits up at once into glyoxyl urea, CO2, and $NH_3 - NH_4HA''aq - KHA'' - K_2A''1\frac{1}{2}aq -$

Ba(HA''), aq minute needles OXYACANTHINE C18H19NO3 the root of Berberis vulgaris, together with berberine, berbamine, and at least one other alkaloid Needles (from alcohol or ether), or amorphous solid In the amorphous state it melts at [138°-150°], in the crystalline state at [208°-214°] V sol benzene and chloroform, scarcely in petroleum spirit In chloroform $[a]_D = +1316$ Conc H_2SO_4 , or conc H_2SO_4 and molybdic acid, gives no colour at first, but on standing or heating, a yellow colour 10dic acid it separates iodine

Salts - B'HCl 2aq small colourless needles, in aqueous solution $[a]_D = +1636$ B'HNO₃ 2aq, colourless needles -B'₂H₂SO₄ 2aq microscopic plates —B'₂H₂SO₄6aq small prisms —B'₂H₂Cl₂PtCl₄5aq yellow pp (Hesse, B 19, 3190, cf Polex, Ar Ph 6, 265, Wacker, J 1861,

DIOXY-ACENAPHTHENE C₁₀H₆<CH(OH) Acenaphthylene-glycol [205°] Formed by sa ponifying its acetyl derivative, which is obtained C₁₀H₀<CHBr from di bromo acenaphthene Ewan a Cohen, C J 55, 578) Long colour less needles, sl sol cold MeOH and hot water On treatment with Na and alcohol it yields the ketone $C_{10}H_6 < \stackrel{CH_2}{<} [119^\circ]$

Mono-acetyl derivative C₁₂H₂AcO₂ [112°] Long needles, v sol alcohol Dr-acetyl derivative C12H8Ac2O2. [130° Benzoyl derivative C12H2BzO2 1907 OXY-ACETIC ACID v GLYCOLLIC ACID Di-oxy-acetic acid v GLYOXYLIC ACID Tri-oxy-acetic acid v Oxalic acid. DI-OXY-ACETOACETIC ETHER

Di-ethyl derivative C10H18Os is CH₂(OEt) CO CH(OEt) CO₂Et (245°) Formed by the action of Na on a solution of CH₂(OEt) CO₂Et in benzene (Conrad, B. 11, 58).

Liquid, gives a violet colour with FeCl. Forms Na and Ba derivatives Split up by alkalis into 'alcohol and CH₂(OEt) CO₂H

OXY-ACETONE v ACETYL CARBINOL

s-D1 oxy acetone Dr ethyl derivative

C,H₁₄O₃ 16 CO(CH₂OEt)₂ (195°) SG 17.5 98 VD 495 Formed by allowing the ether CH2(OEt) CO CH(OEt) CO2Et (v the preceding article) to stand for three days with cold dilute (25 pc) KOH, neutralising with H2SO, extract ing with ether, and distilling (Grimaux a Lefèvre, CR 107, 914) Sweet aromatic liquid, sl sol Aq, sol alcohol, volatile with steam Combines with NaHSO, Reduces Fehling's solution and yields a mirror with warm ammoniacal AgNO.

u Di oxy acetone v Pyruvic aldehyde

p OXY ACETOPHENONE C.H. (OH) CO CH. [1 4] [107°] Obtained by diazotising p aimido acetophenone and boiling the solution (Klingel, B 18, 2691) Formed also by heating phenol with ZnCl₂ and HOAc (Michael a Palmer, Am 7 White needles Sol water, alcohol, and ether FeCl₃ gives a dark brown colouration

Methyl derivative C.H. (OMe) CO CH. [89°] (Gattermann, B 23, 1201) (258°) (G), (221°) (O) Formed by heating anisic aldehyde with Na and MeI in ethereal solution (Oliveri,

G 13, 275)

Ethyl derivative [61°] (above 260°) w Oxy acetophenone v BENZOYL CARBINOL way acetophenone v BENOYL CARBINOL
The phenyl derivative Br CH₂(OPh) [72°]
and the p nitro-phenyl derivative
Bz CH₂(OC₂H,NO₂) [144°] may be obtained from
ω bromo acetophenone (Mohlau, B 15, 2497)
The phenyl hydiazides C₂H, C(N₂HPh) CH₂OH
[112°] and C₂H, C(N HPh) CH N₂HPh [152°]
have been preserved by Leubmann (A 242 247) have been prepared by Laubmann (A 243, 247).

(4 2 1) Di oxy acetophenone [4 2 1]C, $H_s(OH)_2$ CO CH_s Resacetophenone [142°] Formed by fusion of β methyl umbelliferon with KOH (Pechmann a Duisberg, B 16, 2123) Prepared by heating resorcin (1 pt) with HOAc (1½ pts) and ZnCl. (1½ pts) at 150° (Nencki a Sieber, J pr [2] 23, 147, 546) Fine white needles Gives a red colouration with Fe Cl. With HOAc, ZnCl., and POCl, it gives (H. (AL) Ac, 1200) (C. 1200) (C. 1200) $C_{\rm e}H$ (OH) Ac, [180°] (Crépieux, Bl [3] 6, 152) Acetyl derivative C.H. (OAc) CO CH,

og (303°) White needles Phenyl hydrazide [73°]

C₆H₃(OH)₂·CMe N₂HPh [139°] Tables (from xylene) (Michael a Palmer, Am 7, 276)

Methyl derivative $[2\ 4\ 1]\ C_6H_3(OH)(OMe)\ CO\ CH_3$ Occurs in Japanese peonies (Will, B 19, 1776) Di ethyl derivative [68°] (G)

(5, 2, 1) Di oxy acetophenone [202°] Made in like manner from hydroquinone (Nencki)

Tri oxy acetophenone CsHsO4 16 C₆H₂(OH)₃ CO CH₃ Gallacetophenone Formed by heating pyrogallol (1 pt) with HOAc (1 pts) and ZnOl, (1 pts) at 150° (Nencki a Sieber, J pr [2] 28, 147, 538) Pearly plates Alcoholio KOH ppts C.H.O.KOH

OXY-ACETOPHENONE-CARBOXYLIC ACID Phenyl derivative C₁₈H₁₂O₄ te C₄H₄(CO₂H) CO CH₂OPh. [110°] Prepared by dissolving C.H. CO CH OPh in alkalis and acidifying the solution. Needles (Gabriel, B. 14, 923) -A'Ag white flocculent pp

β-OXY-ACETYL PROPIONIC ACID

C₃H₁(OH)O₃, \$\beta\$-Oxy-levulic acid Formed in chief quantity, together with acetacrylic acid, by the action of aqueous Na₂CO₃ upon \$\beta\$-bromo-levulic acid. Yellowish oil V sol water and alcohol, sl sol other solvents Very prone to enter into reactions Reduces alkaline silver solutions Hydroxylamine gives an oxim [145°] By heating with NH, it yields tetra-methylpyrazine (di-methyl ketine), with evolution of CO₂ The salts are amorphous and easily de composable (Wolff, B 20, 426, A 264, 234) On heating it yields two anhydrides [240°] and [263°]

The isomeric a-oxy acetyl propionic acid CH₂Ac CH(OH) CO₂H [104°] is crystalline

OXYACIDS v vol 1 p 57

OXY-ACRYLIC ACID v GLYCIDIC ACID and PYRUVIC ACID

OXY-ADIPIC ACID C.H.O. 2 e CO₂H CHMe CMe(OH) CO₂H Formed by treating methyl-acetoacetic ether with HCy and boil ing the product with HClAq (Konig, B 12, 768) Crystalline mass —Na₂A" —Àg A"

Isomeride v Adipomalic acid

Di-oxy-adipic acid CaH10Oa Formed by the action of Ag₂O on the di bromo adipic acid prepared from hydromuconic acid (v p 443) (Lim pricht, A 165, 267) Syrup, sol alcohol and ether -BaA" 4aq hygroscopic powder

Di-oxy-adipic acid Got from its nitrile, which is formed by warming the anhydride C, H, O, of erythrite with dry HCy at 55° (Przybytek, B 17, 1094) Crystalline — KHA" — CdA" 4aq

PbA" 2aq amorphous pp

Tri-oxy-adipic acid C_cH₁₀O, Prepared by boiling tri bromo adipic acid with baryta water (Limpricht) Prisms (from alcohol benzene) -BaA" aq v sol water

Tri-oxy-adipic acid $C_6H_{10}O_7$ [147°] Formed by oxidising metasaccharin with HNO₁ (S G 1 2) at 50° (Kılıanı, B 18, 644, 1555) Small mono olinic plates, v sol water, v sl sol alcohol and ether Reduced by HI to adopte acid [149°] - CaA" 4aq —ZnA" 3½aq —CuA" 4aq —Ag₂A"

Tetra-oxy-adipic acid v Mucic Acid and Sac-CHARIC ACID

OXY-ALDEHYDO-BENZOIC ACID v ALDE-HYDO OXY-BENZOIC ACID

OXY-ALDEHYDO-CYMENE v CARVACROTIC

OXY-ALDEHYDO-PHENOXY-ACETIC ACID Methyl derivative

 $C_6H_3(OMe)(CHO) O CH_2 CO_2H [2 4 1]$ Prepared by melting chloro acetic acid with vanillin, adding aqueous KOH (S G 12), and heat ing on the water bath (Elkan, B 19, 3054) Slender needles (from water), v sol alcohol and ether —AgA' white pp OXY-TRI-ALDINE v ALDEHYDE

OXYAMENYL-NAPHTHOQUINONE v. LA-

PACHIC ACID

OXY-AMIDO-ACETIC ACID C.H.NO. 16. CH(NH₂)(OH) CO₂H Formed by the action of alcoholic NH, on glyoxylic acid (Böttinger, A Syrup -CaA'2 insol cold water.

Yields pyrrole on distillation OXY-AMIDO-ACETOPHENONE-OXIM v Ox-

AMIDO ACETOPHENONE-OXIM

(a) OXY-AMIDO-ANTHRAQUINONE C,H, C,O, C,H,(OH)(NH,) [1 2 4 3] together with a smaller quantity of the (B) 180meride by heating alizarin with NH2Aq for 8 hours at 200° (Liebermann a Troschke, A 183, 202) Brown needles (from alcohol) with green lustre, insol water Yields alizarin on fusing with potash, and on heating with HClAq at 250°.—BaA'₂.

Acetyl derivative C14HeO2(OH)(NHAc). [170°] Formed by heating with Ac.O for 2 hours at 120° (Von Perger, J pr [2] 18, 143) Yello meedles (from HOAc), insol water, sol alkalis Ethyl ether C₁H_eO₂(OEt)(NH₂) [182° Yellow

Red plates (Liebermann a Hagen, B 15, 1796)

 $(\tilde{\beta})$ -Oxy-amido-anthraquinone $\mathbf{O_{e}H_{4}} \, \mathbf{O_{2}O_{2}} \, \mathbf{C_{e}H_{2}(OH)(NH_{2})} \, [1 \, 2 \, 3 \, 4]$ Formed by boiling di-amido anthraquinone with KOHAq Von Perger. J pr [2] 18, 139) Brown needles (Von Perger, J pr [2] 18, 139) Brown needles (from alcohol), insol. water, sol H₂SO₄ Begins to sublime at 150° On boiling with baryta it yields an insoluble Ba salt (difference from the (a)-isomeride) Its solution in KOHAq deposits the K salt on standing Potash fusion forms alizarin Elimination of NH2 yields erythrooxy anthraquinone

Acetyl derivative C14H6O2(OH)(NHAc) Small brownish needles (from alcohol) [242°]

Oxy-amido-anthraquinone

C₁₄H₆O₂(OH)(NH₂) [301°] Prepared by heating sodium anthraquinone sulphonate with NH3Aq at 180° (Bourchart, B 12, 1418) Red needles Yields the tri acetyl derivative C₁₀H₆Ac₃NO₃

Oxy-amido-anthraquinone

C₁₄H₆O₂(NH₂)(OH) Formed by heating purpuroxanthin with NH3Aq (Liebermann, A 183, 217)

Brown needles with green lustre Di-oxy-amido-anthraquinone C₁₄H₃(OH)₂NH₂. (a) Amido alizarin Formed by reducing (a)nitro alizarin with sodium-amalgam (Perkin, C J 30, 578) Crystallises from alcohol in black needles with green lustre Its alcoholic and alkaline solutions are crimson

Di-oxy-amido-anthraquinone C14H5(OH)2NH, (β)-Amido alizarin [above 300°] Formed by reducing (8) nitro alizarin with zinc dust and KOH, or with glucose and H₂SO₄ (Schunck a Roemer, B 12, 588, Brunner a Chuard, B 18, 445) Lustrous red prisms, sl sol alcohol, forming a reddish-yellow solution Its alkaline Dyes iron mordants grey, and solution is blue alumina red

Acetyl-ethenyl derivative

$$C_{\bullet}H_{\bullet} < \stackrel{CO}{CO} > C_{\bullet}H(OAc) < \stackrel{O}{N} > C CH_{\bullet}$$
 [240°]

Formed by heating amidoalizarin with acetic anhydride Yellowish brown crystals (from benzene or acetic anhydride), sublimes in small yellow plates By boiling with HCl it is reconverted into amidoalizarin

Di-acetyl derivative

C,H, CO C,H(OH)(OAc)(NHAc) [268°-271°].

Formed by boiling the preceding body with dilute acetic acid till dissolved Red-brown crystals, soluble in alcohol with a yellow colour Alcoholic Pb(OAc), gives a violet pp, alcoholic Cu(OAc), a red solution It dissolves in aqueous Na₂CO₂ with a violet, in KOH with a blue, colour Alumına-mordants are dyed a deep red

Bensoyl-bensenyl derivative

 $C_{\bullet}H_{\bullet} < \stackrel{CO}{<_{CO}} > C_{\bullet}H(OBz) < \stackrel{O}{>_{N}} > COH_{z}$ [above 800°]

Formed by heating amidoalizarin with benzoyl chloride Small glistening needles, sublimes in yellow needles, nearly insol all solvents Alcoholic KOH gives a blue solution on boiling (Roemer, B 18, 1666)

D1-oxy-amido-anthraquinone

C14H2O2(OH)2(NH2) Amidoisoanthraflavic acid Formed by heating anthrapurpurin with ammonia at 150°-180° (Perkin, C. J. 33, 216) Darkgreen crusts (from alcohol), almost insol water Its alkaline solution is purple Nitrous acid converts it into isoanthraffavic acid

Tetra-amido-di-oxy-anthraqui...one

C₁₄H₂O₂(NH₂)₄(OH)₂ Hydrochrysamide Formed by reducing tetra intro di oxy anthraquinone (chrysammic acid) (Schunck, A 65, 234, Stenhouse a Miller, A 142, 91, Liebermann, A 183, 182) Bluish black needles with coppery lustre, insol boiling water, al sol hot alcohol Its alkaline solution is blue

(a) OXY-AMIDO-ANTHRAQUINONE

PHONIC ACID C14H5O2(OH)(NH2)SO3H Formed from (a) oxy amido anthraquinone and H_2SO_4 at 180° (Von Perger, J pr [2] 18, 182) Brick-red crystalline aggregates (from alcohol) V sol water, giving it a reddish brown colour Insol ether Forms a violet solution with NaOH, a violet-blue pp with baryta water, and a reddish brown pp with BaCl, Dyes, with iron mordant, a pale brown With N2O, it gives oxy anthraquinone sulphonic acid

β Oxy-amido-anthraquinone sulphonic acid Formed from amido erythro oxy-anthraquinone and H₂SO₄ at 115° Crystals obtained from water exhibit a green metallic lustre Aqueous solutions are red Insol ether Forms a purple solution with NaOH, a reddish violet pp with baryta water and a violet red pp with BaCl₂ Dyes, with iron mordants, yellow With N₂O₂ it gives erythro-oxy anthraquinone sulphonic acid

Oxy-amido-anthraquinone sulphonic acid Got by heating sodium anthraquinone disulpho nate with NH3Aq at 180° (Bourchart, B 12, 1419) Violet pp, forming a red solution in ammonia —NH, A' 2½ aq

Di oxy-amido-anthraquinone sulphonic acid C14H4(OH)2(NH2)SO2H Formed by the action of boiling alkalı upon the anhydride C28H16N2S2O9 or the sulphate, which are got by heating (a) nitro-anthraquinone sulphonic acid with H SO. at 200° (Claus, B 15, 1522, 16, 903, Lifschutz, B 17, 902) Red powder with green lustre Decomposed by heat Its alkaline solution is bluish violet

OXY-AMIDO-AZO- v Azo-

OXY-AMIDO-BENZENE v AMIDO PHENOL.

Di-oxy-amido-benzene v Amido Hydroquin one, Amido pyrocatechin, and Amido resorcin D1-oxy-d1-amido-benzene v D1 amido hydro QUINONE and DI AMIDO RESORCIN

Tri-oxy-tri-amido-benzene Tribensoyl de rivative C₆(OH)₃(NHBz)₃[1 3 5 2 4 6] Tribens oyl tri-amido phloroglucin [c 156°] Got by the action of NAOEt on hippuric ether (Rugheimer, B 21, 8329) Needles (containing lgaq), v sl sol water — Cu,A", — Pb,A",
Tetra oxy amido-benzene

C₆H(OH)₄(NH₂)[1 2 4 5 6] Formed from nitro di oxy quinone, SnCl, and HCl (Nietzki a. Schmidt, B 22, 1661) —B'HCl aq needles. Penta - acetyl derevative. [242°].

Tetra-oxy di amido benzene C₆(NH₂)₂(OH)₄ Formed by reduction of nitramilic acid or of nitro-amido tetra oxy benzene with an excess of SnCl₂, the yield is 90 pc of the theoretical The base could not be isolated, being readily oxidised to di-imido di oxy quinone C₆(NH)₂(OH)₂O₅ By HNO₄ it is converted into benzene-tri-quinone C₆O₆ By boiling with KOH, NH₃ is evolved with separation of a black crystalline substance, if this is boiled with water and evaporated with a little KOH, it yields crocomic acid C₅H₂O₅. Distillation with zinc dust yields p phenylene-diamine Hydrochloride C₆(OH)₄(NH₂)₂H₂Cl₂, colourless needles

Dr acetyl derivative Needles

Hexa acetyl derivative

C_c(NHAc)₂(OAc)₄ [c 240°], small colourless tables (Nietzki a Benckiser, B 18, 502, 19, 2727, 21, 1852)

OXY-AMIDO BENZENE SULPHONIC ACID

v Amido phenol sulphonic acid

Di oxy amido benzene sulphonic acid

C₆H₂(OH)₂(NH₂)(SO₃H) Amido resorcin sulphonic acid Formed by reducing the nitroacid (Hazura, M 4, 613, Brunner a Kramer,

B 17, 1870) Plates, with greenish lustre, sl

B 17, 1870) Plates, with greenish lustre, si sol hot water Its alkaline solution soon becomes blue, then green, and finally black

OXY-AMIDO-BENZOIC ACID C,H,NO, te C₈H₁(OH)(NH₂) CO₂H [2 5 1] Amido-saticylic acid Mol w 153 Obtained by reducing the nitro- acid (Beilstein, A 130, 243, Hubner, A 195, 18) Obtained also by reducing C₁₀H, N₂ C₆H₄(OH)CO₂H (F F Frankland, C J 77, 748) and C₆H, N₂ C₆H₄(OH) CO₂H (Impricht, B, 22, 2908) Satiny needles, insol alcohol, sl. sol hot water FeCl₃ colours its aqueous solution cherry red Reactions—1 Distillation produces p amido-

phenol —2 Nutrous acid forms diazo salicylic acid $C_0H_3(OH) < \frac{N_2}{CO} > 0$, which is converted by cone HI into 10do salicylic acid $C_0H_3I(OH)CO_2H$ [193 5°] (Frankland) —3 Urea forms, on heating, crystalline uramidosalicylic acid $C_0H_3N_2O_4$, which at 200° forms 'carboxamidosalicylic' acid $C_1H_3N_2O_4$, (Griess, J pr [2] 1, 235)

Salts — HA'HCl — HA'HSnCl, (Goldberg, J pr [2] 19, 362) — HA'HI (Schmitt, J 1864, 383, 423) — H₂A'₂H₂SO, aq prisms — CAA'₂5¹/₃aq — BaA'₂4aq Needles, v sol water — MgA'₂8aq — ZnA'₂10aq needles (Wattenberg, B 8, 1221)

Acetylder water Och (OH) (NHAO) CO2H.

[218] Thick needles (containing 2aq), v solwater

Benzoyl derivative

C₆H₃(OH)(NHBz)CO₂H [252°] Yields the salts BaA'₂ 6aq and CaA'₂ (Dabney, Am 5, 22)

Oxy-amido-benzoic acid

C_aH₂(ÔH)(NH₂)(CO₂H) [2 3 1] Formed by reducing the intro acid (Hubner, A 195, 17) — HA'HCl aq needles, v sol water

Bensoyl derivative [189°] Needles
Oxy-amido-benzoic acid

C_sH_s(ŎH)(NH₂)CO₂H [5 2 1] [235°] Formed from benzene-azo-m-oxy-benzone acid and SnCl₂ (Limpricht, A 263, 234) Prisms, v. sl solwater—HA'HCl white needles

Oxy-amido-benzoic acid C_aH₁(OH)(NH₂)CO₄H[4 8 1]. Got by reducing

nitro-p oxy benzoic acid (Barth, Z 1866, 648; Deninger, J pr [2] 42, 553) Needles — $H_2A'_2H_2SO_4$ needles, m sol water.

Ethyl ether EtA' Plates

MethylderivativeC,H₃(OMe)(NH₂)CO₂H.

Amido anisic acid [181°] S 125 at 100°

Formed by reducing C₆H₃(OMe)(NO₂)CO₂H.

(Zinin, A 92, 827, Cahours, A Ch [3] 53, 322)

—AgA' curdy pp —HA'HCl —H₂A'₂H₂PtCl₂—

HA'HNO₂ — H₂A'₂H₂SO₄ — Ethers MeA' —

(Me 4')₂H₂PtCl₄ reddish prisms —EtA' —

EtA'HCl —(EtA')₂H₂PtCl₅ brownish-red prisms

Oxy amido-benzoio acid Methylderiva tive C.H.(OMe)(NH.)(CO.H) [42 1] Formed from C.H.Br(OMe)(NH.)(CO.H) by treatment with zino and HCl (Balbiano, G 14, 247). It melts

at 204°.

Oxy-di-amıdo-benzoic acid

C₅H₂(OH)(NH₂) CO₂H [2 3 5 1] Formed by reducing C₅H₂(OH)(NO₂)₂CO₂Me with HI and P (Saytzeff, A 133, 321) Small needles, sl sol cold water — HA'H₂Cl₂. — HA'H₂I₂1½aq — HA'H₂SO₄aq dimetric prisms, sl sol water

Di-oxy-amido benzoic acid Di-methyl derivative C₆H₂(NH₂)(OMe)₂CO₂H Formed with evolution of CO₂ by reduction of nitrohemipic acid C₆H(NO₂)(OMe)₂(CO₂H)₂ with tin and HCl (Grune, B 19, 2305)—A'HHCl white needles

Di-oxy-amido benzolo acid Di-methyl derivative [4 3 x 1] C₆H₂(OMe)₂(NH₂)CO H Amido veratric acid Formed by reducing nitro veratric acid (Tiemann a Matsmoto, B 9, 942, 11, 135) Tables Ethyl ether EtA' [89°]

Di-oxy-amido-benzoic acid Di-methyl derivative C₂H_{*}(OMe)₂(NH₂)CO₂H [5 3 4 1] [182°] Got by reduction (Meyer, M 8, 432) Six sided prisms (from alcohol)—CuA'₂ 2aq—HAHCl needles, m sol cold water

Di oxy-amido-benzoic acid Acetyl-methylene derivative of the Nitrels C₆H₂(O₂CH₂)(NHAc) CN [216°] Formed from the oxim of amido piperonal, Ac₂O, and NaOAc (Haber, B 24, 626) Yellow needles (from chloroform)

Reference—BROMO OXY AMIDO BENZOIC ACID DI-OXY-AMIDO-BENZOIC ALDEHYDE Oxim of the methylens derivative C_cH₂(O₂CH₂)(NH₂) CH NOH [175 5°] Got by reducing the oxim of o-nitro piperonal with am monium sulphide (Haber, B 24, 625) Yellow plates Yields a di acetyl derivative [188°]

OXY-AMIDO-BENZYLAMINE Methyl derivative C₀H₂(OMe)(NH₂)CH₂NH₂ [1 2 4] Formed from C₀H₂(OMe)(NO₂) CH₂NHAC, tin, and HClAq (Goldschmidt a Polonowska, B 20, 2412)—B'HCl needles—B'₂H₂PtCl₂ plates
Di-acetyl derivative [185°] Needles

Di-acetyl derivative [185°] Needles a OXY-β AMIDO-BUTYRIC ACID C.H.NO. i.e. CH. CH(NH₂) CH(OH) CO.H. S 4 at 15° Formed by heating β-methyl glycidic acid in sealed tubes with NH₂Aq at 100° (Pavloff, Bl. [2] 43, 115, Melikoff, J. R. 16, 525) Prisms, with sweet taste

Oxy-amido-isobutyric acid S 55 at 15°. Formed from a-methyl-glyculic acid and NH,

OXY-AMIDO CINNĂMIC ACID Methyl derivative

[5 2 1] O.H. (NH.) (OMe) CH CH CO.H. [189°]. Formed by reduction of nitro-methoxy-cinnamic

acid with FeSO₄ and NH₅ (Schnell, B 17, 1384). Colourless needles V sol alcohol and ether, almost insol cold water An aqueous solution of the ammonium salt gives pps with AgNO₅, CuSO₄, Pb(OAo)₂, and ZnSO₄

 $\begin{array}{cccc} Anhydrade C_{\rm e}H_{\rm 3}({\rm NH_2}) & \stackrel{\rm O~CO}{\rm CH~OH} & Amidocoumarin & [170°] & (Frapolli a Chiozza, A 95, 253), [161°] & (Taege, B 20, 2110) & Got by reduction of nitro coumarin <math>-B'_{\rm 2}H_{\rm 2}PtCl_{\rm g} \end{array}$

Di-oxy-amido cinnamic acid Methylene derivative.

 $CH_2 < {0 \atop 0} > C_6H_2(NH_2)$ CH CH CO₂H. [207°]

Formed by reducing the nitro-acid with NH, and hot aqueous FeSO₄ (F M Perkin, C. J 59, 158) Brownish needles, v sol HOAc

DI OXY-AMIDOETHYL BENZOIC ACID Methylene derivative $C_{10}H_{11}NO_4$ is C_6H (O.CH₂)(CH₂CH₂NH) (CO₄H wAmido ethylproeronylearboxylic acid' [182°] Formed, together with hemipic acid, by boiling anhydro berberilic acid with water (W H Perkin, jun, C J 57, 1055) Needles, sl sol alcohol, m sol cold water — (HA')₂H₂SO₄2aq [203°] — Colourless prisms—HA'HCl—HA'H,CO, [203°]— (HA')₂H₂PtCl₆ [222°]—HA'HAUCl₃

Di-benzoyl derivative $C_{2i}H_{19}NO_{e}$ [150°] $Anhydride CH_{2} \stackrel{\bigcirc}{\bigcirc} C_{6}H_{2} \stackrel{\bigcirc}{\subset} CH_{2} CH_{2}$

Formed by heating the acid, and, along with its ψ opianate and ψ opianic acid by the action of alkalis on berbeial It is also a product of the oxidation of berberine with KMnO, Yields the compound $C_{in}H_sBrNO_s$ [240°]—Opianate B'C,H (OMe),(CO,H)₂ [132°]— ψ Opianate $C_oH_{is}NO_s$ [142°] Needles, sl sol cold water Yields berberal when heated

OXY AMIDO GLUTAMIC ETHER C,H₁₄N₂O₄ te CO(NH₂) CH₂ C(OH)(NH₂) CH₂ CO₂Et [86°] Formed from acetone dicarboxylic ether and conc NH₂Aq (Stokes a Von Pechmann, B 19, 2694) Needles, sl sol cold water, insol alkalis FeCl₂ gives a red colour Dilute HClAq yields a body melting at 61° turned purple by FeCl₂ Nitrous acid yields a nitroso derivative [178°] Boiling alkaline carbonates yield glutazine (v

DI OXY AMIDO PYRIDINE)

OXY AMIDO-HEPTOIC ACID C,H₁₈NO₃ ve CMe₂(NH₂) CH₂ CMe(OH) CO.H Amidotrimethylbutyllactic acid [210°] Formed by the action of boiling baryta water on its anhydride which is obtained by the action of boiling conc HClAq upon the product of the union of HCy with diacetonamine (Heintz, A 189, 231, 192, 329, Weil, A 232, 208) Prisms (from water), insol alcohol and ether Neutral to litmus Yields its anhydride when heated—Salts CuC,H₁₃NO₂2aq minute greenish blue prisms—(HA)₂H₂SO₄—HA'HCl crystalline

Anhydride CMe(OH) CONH Or oxy
bri-methyl-pyrrole Prisms (by sublimation)

Melts above 180°

OXY-AMIDO HYDRO ISATIN v ISATIN OXY-AMIDO-IMIDO-DI PHENYL SUL-

PHIDE C₁₂H₈N₂SO s.e OC₆H₁ S.

Thionoline Formed by adding H₂S and

Thronoline Formed by adding H_2S and N $C(NH_2)$ FeOl successively to an aqueous solution of p. Obtained by reduction of nitro (β) naphtho-

amido phenol hydrochloride (Bernthsen, A. 280, 202) Yellowish brown plates or needles with green lustre (from alcohol)

OXY-AMÎDO-DI-ISATÎN DIAMÎDE ISATÎN DI-OXY-DI AMÎDO-TETRAMETHENYL

Dr-benzoyl derivative C(NHBz) C(OH) = C(NHBz) [188°] Formed by heating hippuric ether with NaOEt, or with Na, at 160° (Rugheimer, B 21, 3325, 22, 114) Needles, m sol alcohol, v e sol benzene FeCl₃ colours its alcoholic solution violet Decomposed by acids into benzoic acid and di amido acetone Hydr xylamine does not affect it Methyl alcohol and gaseous HCl form a body $(C_{11}H_{10}N_2O_3?)$ crystallising in plates [200°]

Oxy-tetra amido-pentamethenyl hydride

CH(OH) C(NH₂) C(NH₂) Tetra amido pentol Formed from the tetra oxim of leuconic acid SnCl₂ and HClAq (Nietzki a Rosemann, B 22, 923)—B¹v3HCl octahedra—B¹v(H₂SO₄)₂ aq

Tetra oxy-tetra-amido octomethenyl Tetra benzoyl derivative $C_{16}H_{08}N_4O_6$ is $C(OH) \leq C(NHBz) C(OH) C(NHBz) > C(OH)$ A product of the action NaOEt on hippuric ether (Rugheimer, B 22, 1962) Small yellow needles Does not melt below $270^\circ - BaC_{36}H_{.6}N_4O_6$ pp

Anhydride C_{3s}H₁N₄O₈
OXY-AMIDO-METHYL-ANTHRAQUINONE
C_{1s}H₁₁NO₁ ve C_{1s}H₃Me(OH)(NH)O₂ Formed
by heating chrysophanic acid with NH₃Aq at
200° (Liebermann, A 183, 218) Brown plates

Oxy-di-amido-methyl-anthraquinone $C_{10}H_{12}N_2O_3$ Di amido chrysophanic acid with excess of NH_3Aq at 150° With Ac O it yields $C_{15}H_{11}AcN_1O_3$ crystallising from chlorotorm in lustrous violet needles

OXY DIAMIDO METHYL-DIPHENYL

 $\begin{array}{c} Ethyl\ derivative \\ \textbf{C}_{\delta}\textbf{H}_{4}(\textbf{NH}_{2})\ \textbf{C}_{\delta}\textbf{H}_{2}\textbf{Me}(\textbf{OEt})(\textbf{NH}_{2})\ [1\ 2\ 5\ 4] \\ \textbf{Formed from the hydrazo}\ derivative} \\ \textbf{C}_{\delta}\textbf{H}_{\delta}\ \textbf{NH}\ \textbf{NH}\ \textbf{C}_{\delta}\textbf{H}_{2}\textbf{Me}(\textbf{OEt})\ \textbf{by dissolving in cold} \\ \textbf{HClAq}\ (\textbf{Noelting a}\ \textbf{Werner},\ B\ 23,\ 3263) \\ \textbf{Needles, v sl sol water} \end{array}$

Oxy di amido methyl diphenyl [3 4 1] $C_6H_3Me(NH_2)$ $C_6H_3(OH)(NH_3)$ [1 3 4] [177°] Formed by the action of water at 180° on the sulphonic acid $C_6H_3Me(NH_2)$ C_6H (OH)(NH)SO $_3H$ [1 3 4 6], got by reducing the dye from diazotised o toluidine and p phenol sulphonic acid (Weinberg, B 20, 3174) Plates, v sl sol water

Ethyl derivative $C_sH_sMe(NH.)$ $C_sH_s(OEt)(NH.)$ [117 5°] Formed in like manner from $C_{1s}H_s(OEt)(NH.)_sO_sH_s$ which yields HA'HCl 4aq and BaA's 8aq

OXY-AMIDO-METHYL QUINOLINE

C₉H₄(OH)(NH₂)MeN Formed by reducing nitro (Py 1)-oxy (Py 3) methyl quinoline (Conrad a Limpach, B 20, 950) Prisms, decomposing at 225° without melting —B'HCl aq

OXY AMIDO NAPHTHALENE v. AMIDO-

(1,2,3)-D1 oxy amido naphthalene

C(OH) C(OH)

C₂H

N
C(NH₂)

Obtained by reduction of nitro (8) naphtho-

quinone (Korn, B 17, 906) Reduces cold AgNO.

Fe.Cl. gives a blue black pp. (2,2',1)-Di oxy amido naphthalene

C(OH) CH C C(NH₂) C(OH). Formed by re-CH CH CCH CH ducing the (a) oxim of (2') oxy (B) naphthoquinone with SnCl. (Clausius, B 23, 521) -B'HCl needles, turning blue in air

Di-oxy-amido-naphthalene Got by reducing amido (a)-napthoquinone (Graebe a Ludwig, A. 154, 320) Tables, v. e sol water Blackens in moist air

Tri-oxy am.do naphthalene

 $C_{c}H_{4} < \stackrel{C(\mathrm{OH})}{<} \stackrel{C(\mathrm{NH}_{2})}{(\mathrm{OH})}$ Formed by reducing nitro oxy (a) naphthoquinone with SnCl₂ (Kehrmann, B 21, 1780, J pr [2] 40, 179) Monoclinic crystals Cold cone HNO₃ appears to form C_eH₄ < CO C(N NO) crystallising in red dish yellow needles Yields a tetra acetyl derivative [145°]

OXY AMIDO NAPHTHALENE SULPHONIC ACID v Amido naphthol sulphonic acid

Oxy di amido nephthalene sulphonic acid $C_{gH_4}(NH_2)_2(OH)(SO_3H)$ [x 4' 1 4] The hydrochloride B'HCl is formed by reducing dinitro naphthol sulphonic acid with SnCl₂ and HCl (Nietzki a Zubelen, B 22, 455) It crystallises in colourless needles

OXY m AMIDO NAPHTHOIC ACID

C10H5(OH)(NH)CO H Formed by reducing the nitro acid (Schmitt a Burkard, B 20, 2700) Decomposes above 200°

Acctyl derivative [185°

Oxy p amido naphthoic acid Got by reducing C, H4(SO,H) N C10H5(OH)CO H with tin and HCl (S a B) Decomposes above 200°

Acetyl derivative [195°].

Oxy amido naphthoic acid C₁₀H (OH)(NH₂)(CO₂H) [1 4 2?] [above 200°] Formed from (a) oxy naphthoic acid by combining it with diazobenzene chloride and warming the product with SnCl and HCl (Nietzki a Guitermann, B 20, 1275) Crystalline powder, insol water Decomposes above 230° into CO2 and (a) amido (a) naphthol

OXY AMIDO (α)-NAPHTHOQUINONE

 $C_{\bullet}H_{\bullet} < CO C(NH)$ Amido - naphthalic acid Formed by reduction from nitro oxy naphthoquinone (Diehl a Merz, B 11, 1319) and from di nitroso di oxy naphthalene (Kostanecki, B 22, 1346) Formed also by oxidising trioxy amido - naphthalene with aqueous FeCl_a (Kehrmann, B 21, 1781) Red prisms, sl sol water Its alkaline solutions are blue -BaA'2: violet pp —AgA' grey pp
Acetyl derivative C₁₀H₄O₂(OH)(NHAc)

[220°] Formed from C₁₀H₄(OAc)₂(NHAc) and KOHAq (Kehrmann a Weichardt, *J pr* [2] 40, 182) Yellow needles, insol water —KA', blueblack needles

Oxem CoH. CONOH C NH. Greenish flocculent pp -B'HCl yellow needles.

Acetyl derivative of the oxim O₆H₄<CO C NHAO Golden needles, sl.

sel alcohol Decomposes at 190°-200°.

OXY DIAMIDO DIPHENYL C12H12N2O 2.6. [41] C₆H₄(NH₂) C₆H₃(NH₂)(OH) [142] [185°]. Formed by the action of water at 180° on the hydrochloride of its sulphonic acid, which is got by reducing C₆H, N₂ C₆H₃(OH)SO₂H with SnCl₂ at 30° (Weinberg, B 20, 3173, Noelting a. Werner, B 23, 3256) Plates, sl sol water -HA'H2SO ınsol water HA'HCl — (HA')2H2PtCl65aq sl sol water

Ethyl derivative $C_6H_4(NH_2)$ $C_6H_3(NH_2)(OEt)$ [135°]. Needles. sl sol water — HA'H2SO, prisms

D1 - oxy - d1 - amido - diphenyl Di-ethylderivative [4 3 1] C₀H₃(NH₂)(OEt) C₆H₃(NH₂)(OEt) [1 4 3] To ethoxy benzulane [117°] Formed from [2 1] C_sH₄(OEt)NH NH C_sH₄(OEt) [1 2] and conc HClAq (Mohlau, J pr [2] 19, 381) Needles or plates, sol hot water —B"H₂Cl. —B"2HSnCl₃ — D'HL DOWN DOWN GRAND FROM SERVICE (100 pt 100 pt B"H PtCl, -B"H,SO, needles, sol hot water

Di oxy di amido diphenyl

[3 4 1] $C_0H_3(NH_2)(OH) C_0H_3(NH_2)(OH)$ [1 3 4] [above 3009] Formed by reducing di nitro di-ovy diphenyl (Kunze, B 21, 3332, Schutz, B 21, 3531) Needles or plates Ac O yields the diacetyl derivative AcCl forms the di ethenyl denivative [195°] —B'H.Cl. needles —B"H.SO. Di-acetyl derivative

 $C_{12}H_6(OH)$ (NHAc), [210°] Needles, alkalis, insol acids

Tetra-acetyl derivative C12H2Ac1N2O2 [225°] White needles (K)

Dı oxy-tetra amıdo diphenyl

 $C_{s}H_{2}(NH_{s})_{2}(OH)$ $C_{s}H$ (NH_{s}) (OH) Formed from tetra nitro di oxy diphenyl (Kunze) Colourless needles or silvery plates, turning blue in air AcCl converts it into a compound C10H14N4O2 -B''H,Cl, 4aq -B''H SO, white needles

Tetra acetyl derivative C₁₂H₄(NHAc)₄(OH)₂ [280°] Got by boiling the hexa acetyl derivative with NaOHAq

Hexa acetyl derivative C_{1°}H₄(NHAc)₄(OAc) [300°] Formed from the base and boiling Ac O

Tetra oxy di amido diphenyl $C_6H_1(OH)_2(NH)$ $C_6H_2(OH)_2NH_{24}$ Tetra-methyl derivative

C₁.H₄(OMe)₄(NH₂) [210°] Formed by molecular change from tetra methoxy hydrazobenzene under the influence of acids (Baessler, B 17, 2128) Silky white needles, v sol chloroform, CS, hot alcohol, and hot benzene, sl sol water and ligroin —B"H Cl, small white, easily soluble needles -B"H Cl₂PtCl₄ yellow pp The di-acetyl derivative forms white needles [251°], sol hot alcohol, benzene, chloroform, and CS

Tetra-ethyl derivative $C_{12}H_4({
m NH_2})_2({
m OEt})_4$ [129°] Formed, in like manner, from the hydrazo-compound got by reducing the di ethyl ether of nitio hydroquinone with powdered zine and alcoholic potash (Nietzki, B 12, 39) Leaflets —B"H₂Ol₂— (Nietzki, B 12, 39) Leaflet B"H₂PtCl_e yellow crystalline pp

Tetra-oxy tetra-amido-diphenyl Tetra-CoH2(NHAc) (OH) derivative acetyl White needles, formed by reduction of the cor responding quinone (C,H(NHAc)2OH)2O2 [268°] which is formed by oxidation of tri-acetyl triamido phenol (Bamberger, B 16, 2403)

. OXY-0 AMIDO-PHENYL-ACETIC ACID Hydrindic acid

Acetyl derivative

C_sH_s(NHAc) CH(OH) CO_sH [142°] Got by reducing acetyl isatic acid with sodium amalgam in presence of acetic acid (Suida, B 11, 586) Needles, v sol water

Anhydride v DI OXINDOLE

p-Oxy-a-amido-phenyl acetic acid Methyl derivative C.H. (OMe) CH(NH) CO2H [225°] Formed from anisic aldehyde by successive treatment with HCy, alcoholic NH₃, and HCl (Tie mann a Köhler, B 14, 1979). Needles (from dilute alcohol) —CuA'₂ blue amorphous pp

Di-oxy a amido-phenyl-acetic acid Methylene derivative CH2O2 C6H3 CH(NH2) CO2H [210°] Formed from piperonal by successive treatment with HCy, alcoholic NH_s, and HCl (Lorenz, B 14, 794) Needles, sl sol water

OXY - AMIDO - PHENYL - ACRIDINE CHRYSOPHENOL

OXY-AMIDO DI PHENYL-AMINE

C₆H₅ NH C₆H₃(OH)(NH₂)[1 3 4] [135°] Formed by reducing nitroso-oxy di phenyl amine (Kohler, B 21, 910) Plates, v sol chloroform

OXY-AMIDO-PHENYL CARBAMICETHERS Formed from the nitro compounds (Köhler, J pr [2] 29, 263)

[4 3 1] C₆H₈(ÓEt)(NH₂) NH CO₂Et Small needles —B'HCl [156°] Needles

[4 3 x 1] C₆H₂(OEt)(NH₂),NHCO,Et Needles -B'HCl [238°] Six sided plates, sol water C.H(OEt)(NH2),NHCO2Et Small needles, oxidising in air -B'HCl rapidly Needles

OXY-AMIDO-DI-PHENYL-METHANE . AMIDO BENZYL-PHENOL

Oxy di amido-tri-phenyl-methane Methyl C.H.(OMe) CH(C.H.NH.)2 derivative Formed by heating anisic aldehyde with aniline and HClAq (Mazzara a Possetto, G 15, 57) Crystalline crust (containing C, H, melting at

Di - oxy - tri - amido - tri - phenyl - methane Di-methyl derivative $C_6H_4(NH_2)$ $CH(C_6H_3(NH_2)$ OMe)₂ [183°] tained by reduction of the di methyl derivative of nitro di-amido-di-oxy tri-phenyl methane (Fischer, B 15, 681) Plates or tables Yields on oxidation 'rosanidine,' a bluish red colouring matter with blue fluorescence

OXY - AMIDO - PHENYL - METHYL - PYR-AZOLE C₁₀H₁₁N₂O is C₆H₅N CO CH(NH₂)

Formed by reducing the nitro compound (Knorr, ▲ 238, 189) Rapidly oxidised by air —B'HCl

OXY DI-AMIDO PHENYL-METHYL-PYR IMIDINE $C_{11}H_{12}N_{1}O$ [232°-240°] Formed from $C_{6}H_{3}CH \underset{N}{\leqslant} N \overset{C(OH)}{\lesssim} CH$ by nitration and $\begin{array}{ll} \textbf{reduction} \; (\textbf{Pinner}, B \; 20, 2364) & \textbf{Golden} \; \textbf{needles}, \\ \textbf{sol} \; \; \textbf{NaOHAq} \; -\textbf{B''H}_2\textbf{PtCl}_8 \; -\textbf{B''H}_2\textbf{I}_2 \quad \textbf{prisms} \end{array}$

OXY-DI-AMIDO-PHENYL NAPHTHALENE Ethyl derivative

[2 1 4] $\check{\mathbf{C}}_{10}\mathbf{H}_{5}(OEt)(NH_{2}) C_{6}\mathbf{H}_{4}NH_{2}$ [1 4] Formed by reducing C.H. N2 C., H. OEt in alcoholic solution with SnCl2 and HCl (Weinberg, B 20, 3177) White flakes —B"HCl —B"H₂ŠO₄ al sol water.

OXY-AMIDO-PHENYL PROPIONIC ACID C_eH₃ CH(NH₂) CH(OH) CO₂H [190°] Formed from sodium phenyl glycidate and NH. (Plochl, B 16, 2822, Erlenmeyer, jun, B 22, 1482) Decomposes at 221° (E)

a Oxy o-amido phenyl propionic acid.

Anhydride C.H. NH CO CH, CH(OH) . Oxyhydro-

carbostyril [198°] Got by reducing the product of the nitration of a-oxy phenyl propionic acid (Erlenmeyer a Lipp, A 219, 229) White plates (from alcohol) Sl sol ether, vosol hot water

α Oxy-p-amido-phenyl-propionic acid C₆H₄(NH₂) CH₂.CH(OH) CO₂H [189°] by reducing the nitrate of nitro oxy phenylpropionic acid (Erlenmeyer a Lipp, A 219, 227) Slender needles (containing laq) from dilute (93 p c) alcohol More sol alcohol or ether than tyrosine Readily soluble in alkalis or acids Unlike tyrosine, its solution is acid and it does not give Piria's reaction Boiled with Hg(NO₃)₂ it forms a yellow flocculent pp, which, on adding HNO₃, turns red HA'HCl V sol. on adding HNO, turns red water or alcohol, without decomposition

p Oxy a amido phenyl propionic TYROSINE

 $\alpha\beta$ -Di oxy-o-amido phenyl propionic acid C₆H₄(NH₂) CH(OH) CH(OH) CO₂H [218°] Produced in the reduction of o nitro cinnamic acid by tin and HClAq (Morgan, J 1877, 788) Yellow needles (from alcohol) Its solutions fluoresce green

Di oxy amido propionic acid Anhydride

of the methylene derivative

 $CH_2 \stackrel{O}{<} C_e H_2 \stackrel{NH}{<} CH_2 \stackrel{CO}{CH_2} CH_2$ 'Ethylamidopiperonyl w carboxylic anhydride' [235°] Formed by reducing (CH₂O₂)C₆H
₂(NO₂) CH CH CO Et in alcoholic solution with tin and gaseous HCl (F M Perkin, C J 59, 159) Crystalline pp

OXY-AMIDO PHENYL PYRAZOLE CARB-OXYLIC ACID

Benzoyl derivative NPh CO CH NHBz [185°-190°] Formed from its ether and NaOH (Wishcenus, B 24, 1261) Yellowish needles, sl sol water

Ethyl ether EtA' [195°] Formed by boiling the phenyl hydrazide of benzoyl amidooxalacetic ether with HOAc Yellow crystals

OXY m - AMIDO PHENYL-PYROTARTARIC

 $\begin{array}{ll} \textbf{ACID} & \textbf{Anhydride} \ \textbf{C}_{11}\textbf{H}_{11}\textbf{NO}_{4} \ \textbf{re} \\ \textbf{C}_{6}\textbf{H}_{4}(\textbf{NH}_{2}) \ \textbf{CH} < \begin{matrix} \textbf{CH}(\textbf{CO},\textbf{H}) \\ \textbf{O} \ \textbf{CO} \ \textbf{CH}_{2} \end{matrix} \end{matrix} > \qquad \textbf{A} \end{array}$ Amidophenyl-Formed by reducing the paraconic acid corresponding intro compound (Salomonson, R T C 6, 18)—B'HCl prisms—B'₂H₂PtCl₂
The isomeric oxy p amido phenyl pyrotartario anhydride yields a similar hydrochloride

(B 2) OXY - p - AMIDO - (Py 3) - PHENYL-

[294°] Formed by passing oxygen over a mix-

ture of (B 2)-oxy-quinoline hydrochloride, aniline hydrochloride, aniline, and platinised asbestos at 220° (Weddel a Georgievitch, M 9, 146) Needles (from amyl alcohol), sl sol. alcohol and ether —B'HCl ½aq —B'2H2SO, 1½aq Acetyl derivative C12H10Ac2N2O. Scales.

(Py 412) Oxy amido phenyl-isoquinoline C(NH₂) CPh

C15H12N2O 200. C6H4 . Amido iso-**^С**(ОН) Й benzal pnthalimidine [c 190°] Formed by red action of the nitro-derivative with P and HI

(Gabriel, B 19, 833) Fine yellow needles

sol acetic acid and hot alcohol

DI-OXY-DI AMIDO-DI-PHENYL PHONE C₁₂H₁₂N₂SO₄ te SO₂(C₄H₂(NH₂)OH)₂ Formed by reducing the nitro-compound (Annaheim, B 7, 436, 8, 1063) Crystals (from Alcoholic isoamyl nitrite forms golden water) plates of $C_{12}H_eN_4SO_4$ Salts $-B'H_2Cl_2$ 2aq $B''H_2I_2$ 2aq $-B''H_2SO_4$ 2aq thick prisms $C_{12}H_{16}Me_2N$ SO $_4H$ I_2 Forms long needles Salts -B"H2Cl2 2aq -Forms long needles -OXY-DI-AMIDO DIPHENYL

SULPHONIC [4 1]C₆H₄(NH₂) C₆H₂(NH₂)(OH)SO₅H₆. Prepared by reducing the azo-com-ACID pound C₆H₅ N₂ C₆H₃(OH)SO₃Na with aqueous SnCl₂ (Weinberg, B 20, 3172, Feer a Muller, C C 1888, 1358) Needles, v sol water —B'HCl

transparent crystals

Ethyl derivative

C₆H₄(NH₂) C₆H (NH₂)(OEt)SO₅H Got in like manner Needles -B'HCl 2aq needles, v sol

OXY-AMIDO-DIPHENYL DISULPHONIC $C_6H_3(NH_2)(SO_9H)C_6H_9(OH)(SO_9H)$ ACID Formed from benzidine disulphonic acid by the diazo reaction (Limpricht, A 261, 315) Lightyellow crystalline mass, v e sol water, insol ether -BaA"8aq reddish-yellow crystals

OXY-AMIDO PHENYL TOLYL KETONE $C_{14}H_{13}NO_2$ te $C_6H_4(NH)$ CO $C_6H_3Me(OH)$ or $C_6H_4(OH)$ CO $C_6H_3Me(NH_2)$. A product of the action of water at 270° on commercial rosaniline (Liebermann, B 16, 1927) Small colourless needles, sol acids and alkalis

Di-benzoyl derivative [193°] Needles DI OXY-AMIDO-PHTHALIC ACID Methyl derivative of the anhydride

 $C_{s}H(OMe)(OH)(CO_{2}H) < \stackrel{CO}{NH} [4 \ 3 \ 2 \ \frac{1}{6}]$ Nor-

[175°] methylazoopianic acid Formed by reducing C,H(NO2)(OMe)(OH)(CHO)CO,H with conc SnCl, and HCl (Elbel, B 19, 2307) Colourless needles, nearly insol ether Yields an acetyl derivative C, H, NO, (OMe) (OAc) [198°], and a di acetyl derivative [105°]

Dimethyl derivative of the anhydride v Amido hemipic acid, vol ii p 672

DI - OXY - AMIDO - PHTHALIDE methyl derivative v Amido Meconin (p 198) and Amido \(\psi \) MECONIN (p 199)

α-OXY β AMIDO PROPIONIC ACID CH (NH) CH(OH) CO,H Amido lactic acid b 15 at 20° Formed from CH Cl CH(OH) CO2H and cone NH, Aq (Melikoff, C C 1881, 354, B 13, 958, 1266, Erlenmeyer, B 13, 1077) Monoelinic prisms -B'HCl needles

OXY AMIDO-ISOPROPYL BENZOIC CMe₂(OH)C₆H₃(NH₂) CO₂H[4 2 1] [158°] Got from the nitro- acid (Widman, B 19, 271) Prisms Yields amido-propenyl benzoic acid on boiling with HClAq

Acetyl derivative [174°] Tables Exo oxy amido isopropyl benzoic acid $CMe_2(OH)C_6H_3(NH_2)(CO_2H)$ [4 3 1] Does not

melt below 270° (Widman, B 16, 2571) Ita acetyl derivative is not melted at 280°

OXY-AMIDO PYRIDINE C₅H₃N(OH)(NH₂) [214°] Got by reducing oxy comazine (Krippendorff, J pr [2] 32, 162) Pyramids (containing

aq), v e sol hot water —B'HCl —B',H_PtCl,
D1-oxy-amido-pyridine NH CO CH, C NH

or N C(OH) CH O NH, Glutazine [c 300°]. Formed by boiling β -oxy- β amido glutamic ether CO₂Et CH₂ C(OH)(NH₂) CH₂ CONH₂ with aqueous Na₂OO₂ (Stokes a Von Pechmann, B 19, 2694, 20, 2655, Am 8, 375) Rectangular plates, m sol hot water, almost insol hot alcohol Gives a deep red colour with FeCl, turning dark green on warming

Reactions -1 Hot HClAq yields tri-oxypyridine — 2 Bromine in excess forms CBr₃ CO CBr₂ CONH₂ [c 148°] — 3 By heating with PCl, (6 to 7 pts) it is converted into a mixture of tri chloro oxy-amido pyridine [282°] and tetra chloro amido-pyridine [212°], together with small quantities of di chloro di oxy amidopyridine [242°] and tri chloro amido pyridine [158°] —4 Yields nitro glutazine [170°-180°] and crystalline di nitro glutazine on treatment with nitrous acid gas With NaNO and acetic acid there is formed the nitro nitrosamine C₅H₄N₂O₂(NO₂)(NO) whence NaC₅H₃N₄O₅ crys tallising in yellow needles, which on warming with NaNO, and HOAc yields the di nitionitrosamine salt NaC, H₂N₃O, a scarlet powder

Salts -B HClaq prisms, v sol alcohol -AgA' plates

Acetyl derivative C₃N₂H₃AcO₂ [285°-290°] Tables, not attacked by hydroxylamine. -NH₄A'aq

Di benzoyl derivative C, N2H, Bz, O, $[216^{\circ}]$ Brownish plates, insol water

DI OXY AMIDO PYRIMIDINE CARBOXY. LIC ACID NH $<_{CO}^{CO}_{C(NH_2)}>C_{CO^2H}$ Formed by reducing the nitro acid (Behrend, A 240, 21) Not affected by boiling potassium cyanate -KA' aq

[260°] (Kohler, A Ethyl ether EtA' 236, 32)

OXY AMIDO-PYROTARTARIC ACID

CH, C(OH)(CO.H) CH(NH.) CO H or CH, C(NH,)(CO,H) CH(OH)(CO,H) citramalic acid S 31 at 18° Amidocitramalic acid Formed from oxycitraconic acid and NH, Aq at 100° (Melikoff a Feldmann, A 253, 92) Monoclinic prisms -B'HCl prisms, v sol water

DI OXY AMIDO-PYRROLE Bensoyl derivative N COH CH NHBz [200 5°]. Got by heating at 140° the product of the action of NaOLt on hippuric ether (Rugheimer, B 22, 1957) Plates (from MeOH), v sol warm water

OXY - AMIDO - QUINIZINE - CARBOXYLIC ACID ? C₁₀H₂N₃O₃ Anhydride of amido oxal-acitic acid phenyl hydrazide Formed by warming the phenyl hydrazide of amido-oxalacetic acid (vol 1 p 169) with conc HSO, White glistening plates Insol hot water and ether, v sl sol hot alcohol Dissolves in alkalis and in cone H.SO₄ Reduces Fehling's solution on gently warming Mercuric salts are reduced in the cold with formation of a deep orange red colouration (Tafel, B 20, 246)

(B 4 1)-OXY-AMIDO QUINOLINE

CH C(NH₂) C CH CH CH C(OH) C N CH C,H,(OH)(NH2)N 1.6 Formed by reduction of sulpho benzene azo oxyquinoline (from diazotised sulphanilic acid and (B 4) oxy quinoline) (Fischer a Renouf, B 17, 1643) Crystalline solid Very oxidisable oxidation it gives quinoline quinone Salts — B"H₂Cl₂—B"H₂SO₄ sparingly soluble needles

(B 2, 4)-Oxy-amido-quinoline

C(OH) CH'C CH CH Obtained by reducing CH C(NH₂) C N CH (B 4, 2)-nitro-oxy-quinoline (Altschal, B**2255**) 2255) Needles (containing 2aq) becoming yellowish green on drying at 100° Its acetyl derivative yields at 235° a crystalline ethenyl derivative

(B 2, 1)-Oxy-amido-quinoline

C(OH) C(NH₂) C CH CH CH—CH—C N CH [143°] Got by reducing the nitroso-compound with SnCl2 and HCl (Von Kostanecki, \bar{B} 24, 153) Radiating needles —B"H2SO,2aq needles

(Py 8)-Oxy amido quinoline v Amido carbo

STYRIL

Oxy-amido-quinoline dihydride v Amido-**MYDROCARBOSTYRIL**

OXY-AMIDO QUINONE Acetyl deriva-C(NHAc) CH C O trve C(OH) [170°] Formed from CHCO tetra acetyl di amido hydroquinone, and FeCl, (Nietzki a Schmidt, B 22, 1657) Golden plates (by sublimation)

 $\mathbf{C_6O_2(OH)_2(NH_2)_2}$ Di oxy di amido quinone [142536] Formed from tetra oxy di-amidobenzene hydrochloride by atmospheric oxidation in presence of aqueous NaOAc (Nietzki, B 21, 1850) Reddish brown needles Yields a crys-

talline di acetyl derivative

OXY-AMIDO SULPHOBENZOIC ACID $C_{s}H_{2}(OH)(NH_{2})(SO_{s}H) CO_{2}H$ [2 5 x 1] Obtained by reducing the nitro- acid (Hubner, B 10, 1701) Needles (containing aq) An isomeric acid, crystallising in needles (containing 3aq) is got by sulphonating (2, 5, 1) oxy amido benzoic acid It yields CaA', 5aq crystallising in nodules

OXY-AMIDO-THYMOQUINONIMIDE v vol.

1 p 186

OXY-AMIDO-TOLUIC ACID

C₆H₂Me(OH)(NH₂)CO₂H [1 2 5 3] Formed from o cresotic acid by combining it with diazobenzene and reducing the azo compound (Nietzki a Ruppert, B 23, 3476) Plates, melting above 300° Yields an acetyl derivative [275°]

OXY-DI-AMIDO-DITOLYL Ethul dersvative [1 8 4] $C_6H_3Me(NH_2)$ $C_6H_2Me(OEt)(NH_2)$ [1 2 5 4] [75°] Formed from the hydrazoderivative and H_2SO_4 (Noelting a Werner, B 23, 3264) Needles al sol water

OXY - ISOAMYL - AMINE C.H.10(OH) NH2. SG. 14 9265 Formed from amylene (158°) chlorhydrin (chiefly consisting of tri-methylethylene chlorhydrin) and NH, Aq (Wurtz, A. Suppl 7, 89, Radziszewski a Schramm, B 17, Oil, v sol water Alkaline in reaction P2O5 forms some terpene -B'2H2PtCl orange crystals.

Di-oxy di isoamyl-amine $NH(C_5H_{10}OH)_2$ SG 14 950 A companies the pre-(250°) ceding base Strongly alkaline syrup, sol alcohol and ether

OXY-AMYL-ANTHRACENE

 $C_eH_e < CO_{CH_{(C_eH_{11})}}^{CO} > C_eH_e$. Amyl hydroanth one [253°] Formed by boiling anthranol with KOHAq, and isoamyl iodide (Hallgarten, B 21, 2508) Yellowish crystals

DI-OXY-AMYL-BENZENE

CHPr(OH) CH(OH) C₆H₅ [82°] Formed from isobutyric aldehyde, benzoic aldehyde, and alco holic potash (Fossek, M 5, 120) Crystals
DI-OXY-DI-AMYL KETONE ANHYDRIDE

 $CH_2 < \frac{CH_2}{CHEt} = 0 > C < \frac{CH_2}{OCHEt} > CH_2$. (209° 1 V) S 26 at 15° Obtained by boiling its carboxylic acid with water (Fittig, A 256, 141) Yields C₁₁H₂₀Br₂O [35°] Carboxylic acid

Got by the action of warm NaOHAq on 'di hexolactone,' an oil formed by boiling the lact one of oxyhexoic acid with alcoholic NaOEt Prisms -NaA' -CaA'2 -BaA'2 (dried at 100°) -AgA' white flocculent pp

OXY AMYL-PHOSPHINIC ACID . Oxy

PENTANE PHOSPHONIC ACID

D1-oxy d1-1soamyl hypophosphorous (C4H, CH(OH))2PO OH [160°] Forme Formed by heating isovaleric aldehyde with hypophosphor ous acid in a current of ${\rm CO}_2$ at 95° (Ville, Bl [3] 2, 202, CR 109, 73) Globular masses of slender needles, v sl sol water Gives off PH, and isovaleric aldehyde on heating -KA' 3aq -BaA'2 aq —PbA'2 5aq granules, v sl sol water OXY-ISOAMYL-SUCCINIC ACID Lact

one paraconic acid [124°] Formed by reducing, with sodium amalgam, the isobutaconic acid $PrCH_2CH < CCO_2H > CH$ [168°] which is got by the action of boiling water on brominated Prepared by heating isobutylitaconic acid valeric aldehyde with Ac2O and sodium succinate at 110° (Fittig, A 255, 97, 256, 103) Thin needles (from water) Boiling baryta water yields C₀H₁₄BaO₅ whence C₀H₁₄Ag₂O₅ -CaA'₂2aq Boiling baryta water -BaA'₂ 3aq -ZnA'₂1 $\frac{1}{2}$ aq -AgA' Ethyl ether EtA' [17°]

[17°] (293°)OXY-ANGELIC ACID

Ethyl derivative [133°] CH₃ C(OEt) CMe CO₂H Formed by heating chlorotiglic acid with NaOEt at 130°-160° (Friedrich, A 219, 357) Prisms

Oxy angelic acid CH, CH CH CH(OH) CO2H Formed by saponifying with HClAq the product of the union of liquid HCy and crotonic aldehyde (Lobry de Bruyn, Bl [2] 42, 159) —BaA'₂ crystalline

Oxy angelic lactones v Angelico lactones OXY-ANTHRACENE v Anthranol and ANTHROL

Di-oxy-anthracene C14Hs(OH) Chrysasol Formed by fusing anthracene (a) disulphonic acid with KOH (Liebermann, B 12, 185) Yellow needles Gives a bluish green colouration with FeCl, or bromine

Acetyl derivative [184°]. Needles.

Di-exy anthracene C₁₄H₂(OH)₂. Flavol [c. 270°] Formed by fusing anthracene (a)-disulphonic acid with KOH at a high temperature (Schuler, B 15, 1808) Yellow crystalline powder, v sol alcohol and ether with blue fluorescence. Its alkaline solution exhibits intense green fluorescence.

Acetyl derivative C₁₄H₈(OAc)₂ [255°]. Di-ethyl ether C₁₄H₈(OEt)₂ [229°]

(8) Di oxy anthracene

 $C_4H_1(OH)$ C_2H_2 $C_6H_3(OH)$ Rufol Got by fusing anthracene (β) disulphonic acid with KOH (Liebermann a Boeck, B 11, 1615) Needles, v sol alcohol with blue fluorescence Its alkaline solution is yellow

Di-acetyl derivative [198°] Colourless leaflets Yields anthrarufin on oxidation

Dr. benzoyl derivative [263°] Needles
Isomerides v Oxanthranol and Oxyanthranol

 $\emph{m-oxy}$ anthracoumarin $\mathbf{C_{1e}H_{s}O_{4}}$ s.s \mathbf{CH} co o

C₆H₄ CO C CH C(OH) [325°] Formed

from s di oxy benzoic acid, cinnamic acid, and $\rm H_2SO_4$ at 60° (Von Kostanecki, B 20, 3142) Yellow needles, sol HOAc

Acetyl derivative [255°] Needles

Di oxy anthracoumarin

CH CO O

C_oH₄ C C C C(OH) Styrogallol Formed

by heating a mixture of cinnamic acid, gallic acid, and H_2SO_4 (Jacobsen a Julius, B 20, 2588, Von Kostanecki, B 20, 3143) Minute yellow needles (from alcohol), not melted at 350°

Dr-acetyl derivative [260°] Needles

(a) OXY ANTHRANOL

C_sH_sCH C_t(OH) C_sH_sOH [202°-206°] Formed by boiling oxy anthraquinone (1 pt), zinc dust (2 pts), and NH_sAq (8 pts) with water (5 pts) (Liebermann a Simon, A 212, 28) Slender needles (from dilute alcohol) Yields a di acetyl derivative [155°]

Oxy anthranol dihydride

C₆H₄ CH₂ CH₂ C₈H₃OH [99°] Got by boiling quinizarin with HIAq (Liebermann a Giesel, A 212, 15) Plates (from alcohol) Its solutions fluoresce greenish yellow Yields o oxyanthraquinone on oxidation FeCl₃ colours its alcoholic solution green Ethylamine forms C₁,H₁₀(OH)(NHEt) [172°] -KC₁₄H₁₁O₂ yellow needles -Ba(C₁₄H₁₁O₂)₂ (dried at 100°) - PbC₁₄H₁₀O₂ Actyl derivative C₁₄H₁₁AcO₂ [138°]

A cety l derivative $C_{l4}H_{11}AcO$, [138°] (A) Oxy anthranol $C_{e}H_{4} < C_{(OH)}^{C(OH)} > C_{e}H_{4} v$ Oxanthranol

D1 oxy anthranol C₆H₄<\(\frac{C(OH)}{CH}\)>C₆H₃(OH)

Decayalizarin Prepared by reducing an ammoniscal solution of alizarin with zinc-dust (Rômer, B 14, 1259) Yellow crystals, sl sol water In solution it is slowly oxidised in the air to alizarin The alkaline solution is greenishyellow

Tru-acetyl derivative [188°] Needles. Exhibits blue fluorescence in solution.

Di oxy-anthranol

C_eH₃(OH) COH COH Decorpsoanthraflavic acid [above 330°] Got in like manner from isoanthraflavic acid (Römer a Schwarzer, B 15, 1040) Golden needles Its alkaline solution fluoresces greenish blue.

Dr-acetyl derivative

 $C_sN_s(OAc) < \stackrel{CO}{CH_2} > C_sH_s(OAc)$. [173°]. White needles, insol alkalis

Di oxy-anthranol

 $C_sH_s(OH) < C_c(OH) > C_sH_s(OH)$ Formed by heating anthraflavic acid with HOAc and tin, and slowly adding HClAq (Liebermann, B 21, 445) Needles Yields a tri acetyl derivative [165°] which fluoresces blue in alcoholic solution

Tri oxy anthranol

 $C_{\bullet}H_{\bullet}(OH) < C_{H} > C_{\bullet}H_{\bullet}(OH)_{2}$ Formed in like manner from flavopurpurin (L) Yellow needles Its alkaline solution exhibits greenish fluorescence It yields a tetra-acetyl derivative [105°]

Tri oxy anthranol C_sH_4 \subset C(OH) \subset $C_sH(OH)_s$.

* Anthragalanthranol 'Formed in like manner from anthragallol (L) Yellowish needles Yields a tetra acetyl derivative [205°]

Tri-oxy-anthranol Tetra-acetyl derivative $C_0H_4 < \stackrel{C}{C}(OAc) > C_0H_2(OAc)_2$ [219°]

Formed by boiling hystazarın (1 pt) with NaOAo (13 pts), Ac.O (12 pts), and zinc dust (3 pts) (Schoeller, B 22, 683) Colourless crystals (from alcohol)

Tri oxy anthranol Tetra-acetyl derivative C₆H₃(OAc) C_C(OAc) C₅H₃(OAc) Two isomeric compounds of this constitution [274°] and [c 240°] are formed from anthraflavic acid, NaOAc, Ac,O, and zinc dust (L)

Tri oxy anthranol C_{1.}H_s(OH), 'Anthrapurpuranthranol' Formed by reduction of anthrapurpurin with HOAc, tin, and HClAq (Liebermann, B 21, 443) Minute leather yellow needles, Yields a tetra acetyl derivative [167°]

Tetra oxy-anthranol

 C_bH_* $C_0(OH)$ $C_bH(OH)_*$ Tri-oxy oxanthranol Formed by atmospheric oxidation of an alkaline solution of 'anthragalanthranol' (L) Violet crystals The penta acetyl derivative [203°] is formed by reducing anthragallol with NaOAc, Ac₂O, and zinc dust (Liebermann, B 21, 1172)

Tetra oxy anthranol Penta-acetyl dervative $C_cH_3(OAc)$ $C_0(OAc)$ $C_cH_1(OAc)_2$ [240°] Formed from flavopurpurin, HOAc, Ac₂O, and zinc dust When the operation is protracted the tetra acetyl derivative [250°-260°] is the chief product

Hexa-oxy-anthranol Hepta-acetyl derivative C,H,(OAo), Obtained from rufigallol (L.) Yellowish crystals, sol alcohol, with blue fluorescence

ones having two hydroxyls in the position occupied by them in alizarin possess tinctorial properties (Liebermann a. Wense, B 20, 862).

Erythro - oxyanthraquinone C14H2O2 s.s. CO C CO CH Mol. w 224 [1919]

Formation -1 By fusing o - brome - anthraquinone with KOH at 150° (Pechmann, B. 12, 2127) —2 Together with its isomeride by heating phenol with phthalic anhydride and H2SO4 (Baeyer a Caro, B 7, 968) -3 By the action of nitrous acid on o-amido anthraquinone (Roemer, B 15, 1798) —4 By passing nitrous acid gas into an alcoholic solution of di-amido anthraquinone or (3) oxy amido anthraquinone (Von Perger, J pr [2] 18, 148) -5 Together with three isomeric di-oxy anthraquinones, by heating a mixture of benzoic acid (120 grms) and m-oxy-benzoic acid (60 grms) with 1200 grms of H₂SO₄ and 120 grms of water for 10 hours at 180°-200° (Luebermann a Kostaneck, B 19, 829) —6 By oxidation of oxy-anthranol dihydride (Luebermann, A 212, 20)

Properties - Orange feathery needles (from alcohol), insol water, sol ether and benzene Yields alizarin on fusion with KOH Insol cold baryta-water, but boiling baryta yields a violet salt Insol NH₂Aq, sol HOAc Its ethereal solution shaken with baryta water forms a violet pp, while the isomeric oxyanthraquinone gives a red solution KOHAq dissolves it with difficulty, forming a brown solution May be sub-

limed at 140° in a current of gas

Acetyl derivative C14H, AcO3 [176°-179° Oxy-anthraquinone C₀H₄ CO C CH C(OH)

[302°]

Formation -1 A by product in the preparation of alizarin by fusing anthraquinone sulphonic acid with KOH or NaOH (Liebermann, B 4, 108, 5, 868, A 160, 141, Simon, B 14, 464) Occurs also in the product of the dry disinllation of sodium anthraquinone sulphonate (A G a W H Perkin, C J 47,680)-2 Obtained also from m bromo anthraquinone by careful potash fusion (Graebe a Liebermann, A 212, 25, Suppl 7, 290) -3 By the action of nitrous acid on m amido anthraquinone

Properties —Yellow needles (by sublimation) Readily soluble in excess of baryta water Its alkaline solution is reddish brown fusion yields alizarin HIAq reduces it to anthrol and anthracene hexahydride Sol NH, Aq, forming a reddish yellow liquid -Ba(C14H2O2)2.

 $-\mathrm{Ba}(\mathrm{C}_{14}\mathrm{H}_7\mathrm{O}_3)_2$ aq

Acetyl derivative [158°] Small needles Formed by acetylation and also by oxidation of the acetyl derivative of anthrol

Ethyl ether C₁₄H₂O₂(OEt) [135°] Sol alcohol Very difficult to saponify (Liebermann a Hagen, B 15, 1798)

Di-oxy-anthraquinone

 $C^{e}H^{4} < CO C CH = CH$ Alızarın Mol. w. 240 [290°] S 034 at 100° (Plessy a Schutzenberger, C R 43, 167) Occurs in madder, the root of Rubia tinctoria, which contains its glucoside C₂₈H₂₈O₁₄ (ruberythric acid), and the glucosides of purpurin, purpurin carboxylic acid, purpuroxanthin, and purpuroxanthin carboxylic acid (Robiquet a Colin, A Ch [2] 84, 225, Runge, J pr 5, 362, Schunck, A 66, 174, 201, 81, 336, 87, 344, P M [4] 5, 410, 495, 12, 200, 270, J pr. 59, 465, Rochleder, A 80, 321, 82,

205, Debus, A 66, 351; Wolff a Strecker, A 75, 1, Wartha, B 3, 545, 673, Willigk, A. 82, 389, Rosenstiehl, A Ch [5] 18, 235, C. R 88, 1194, Wurtz, C R 96, 465, Liebermann, B 20, 2241, Bergami, B 20, 2247

Formation -1 By fusing di bromo-anthraquinone with potash (Graebe a Liebermann, 8%). [2] 11, 516, A Suppl 7, 300) -2 By fusing anthraquinone sulphonic acid with potash (Perkin, C J 23, 133, B 9, 281) The yield may be improved by addition of KClO₃ -3 By heat ing pyrocatechin with phthalic anhydride and H₂SO₄ at 140° (Baeyer a Caro, B 7, 972)

Purification -1 By repeat d solution in NaOHAq and ppn by CO₂, the pp being de composed by HCl (Liebermann a Troschke, B 8, 379) —2 Crude commercial alizarin, a mix ture of alizarin, flavo purpurin, and isopur purin, is fractionally sublimed when the alizarin comes over from 100° to 160°, and a mixture of flavo purpurin and isopurpurin from 160° to 170°, the crystals of these two bodies can be distinguished in the sublimate with a microscope and can be separated by means of benzene, in which isopurpurin is only slightly soluble, but the flavo purpurin very soluble (Schunck a Römer, B 13, 41)

Properties - Red trimetric needles, v sol alcohol and ether Sometimes crystallises in golden scales (containing 2aq (Schunck) solutions in alkalis and alkaline carbonates are purple BaCl₂ and CaCl₂ give purple pps in these solutions Alumina decolourises its alco holic solution forming a red lake Salts of Mg, Fe, Cu, and Ag give purple pps in the am

moniacal solution

Reactions -1 Yields phthalic acid on oxida tion with HNO₃ -2 Distillation with zinc dust yields anthracene (G a L) -3 Zinc dust and ammonia reduce it to di ovy anthranol -4 Aqueous ammonia at 200° gives oxy amido anthraquinone, di amido anthraquinone, and other bodies (Von Perger, J pr [2] 18, 129) Salts —CaA"aq —BaA"aq (dried at 100°)

-PbA" violet brown pp

Di-acetyl derivative [160°] (P), [179°-183°] (Baeyer, B 9, 1232) Pale yellow crystals (Perkin, C J 26, 21)

Methyl ether C14H6O2(OH)(OMe) From alizarin, KOH, and MeI (Schunck, C N 27,

Di-ethyl ether C14H6O2(OEt) Got by heating alizarin with KEtSO, and KOH at 170° (Habermann, M 5, 228) Needles

Bromo alizarin v vol 1 p 599

Chloro alizarin v vol 11 p 102 Nitro alizarin v Nitro di OXY ANTHRAQUIN-ONE

Amido alizarin DI OXY AMIDO ANTHRA QUINONE

Alizarin blue C₁₇H₈NO₄ te CO CO CO(OH) C(OH) O N=CH [270°] Formed by heating (3) nitro alizarin (1 pt) with glycerin ($1\frac{1}{2}$ pts) and H_2SO_4 (5 pts) at $107^{\circ}-200^{\circ}$ (Prudhomme, Bl [2] 28, 62, Auerbach, O J 35, 799, Graebe, A 201, 333, B 12, 1416) Brown needles Alkalis form a blue solution, but excess of alkalı throws it down again Dyes chromium acetate mordant blue Yields C₁₇H,NO₂(OH)NH₂ [255°] Gives anthraquinol-

ine when distilled with zinc dust -B'HCl.- | B'HOAc —B'C,H₂(NO₂),0H [245°] —
Ba₂OC₁₄H,NO₄ had greenish-blue pp
Di acetyl derivative C₁,H,Ac₂O₄ [225°]

Dr venzoyl derivative [244°

Alizarin blue $S C_{17}H_{11}NO_4(SO_2Na)_2$ Prepared by dissolving alizarin-blue in a cold con centrated solution of NaHSO, (Brunck a Graebe, B 15, 1783) Reddish brown crystalline powder V sol water, sl sol 95 pc of alcohol it begins to decompose into its constituents

Isoalizarin occurs in madder that has been heated with HClAq or dilute H2SO4 (Rochleder, B 3, 292) Its alkaline solutions are blood red, and it forms a red solution with baryta water It does not dye mordants

p Di-oxy-anthraquinone

CeH CO C C(OH) CH Quinizarin [195°]

Formed by heating hydroquinone or p chloro phenol with H_2SO_4 and phthalic anhydride at 140° (Grimm, B 6, 506) Red needles (from alcohol) Its alkaline solutions are blue Yields anthracene on distillation with zinc dust ethereal solution shows greenish yellow fluor Baryta gives a bluish violet lake discd by MnO, and H2SO, at 140° to purpurin (Baeyer a Caro, B 8, 152)

Reactions -1 HI (S G 17) and a little red

 $\mathcal{C}(OH)$ P give a dihydride, CaH C,H2(OH)2, Ċ(OH)

which forms golden plates or needles (from alco It forms with NaOH a yellow solution, turned blue by air SnCl2 and HCl also reduce quinizarin to this dihydride (Liebermann, A 212, 11) -2 A longer treatment with HI forms hydroquinizarol, $C_{14}H_{12}O_3$ It forms orange modeles (from alcohol) This body is probably $C_bH_4 < C_{CH_2}^{CH(OH)} > C_bH(OH)_2 - 3$ Conc HI (S G 19) and red P after an hour's boiling reduce

quinizarin to oxy anthranol dihydride $(q \ v)$ Di acetyl derivative [200°] Prisms Ethyl ether $C_{14}H_6O_2(OH)(OEt)$ [151°] Drethyl ether $C_{14}H_6O$ (OEt) [177 [1770]

Yellow needles (Liebermann, B 21, 1168)

m D1-oxy-anthraquinone

 $C^{\circ}H^{1} < CO C CH = C(OH)$ Purpuroxanthin Xanthopurpurin [265°] Occurs, together with its carboxylic acid, in madder (Schutzenberger, Bl 4, 12) May be got by reducing purpurin with HIAq or with SnCl2 and NaOH Formed also by dissolving P in a hot alkaline solution of purpurin (Rosenstiehl, C R 79, 764), by the action of introus acid on purpuramide (di-oxy amido anthraquinone) (Liebermann a Fischer, B 8, 974), and, together with anthrachrysone, by heating a mixture of s-dioxy benzoic acid (1 pt), benzoic acid (5 pts), and H₂SO, at 105°-110° (Noah, B 19, 332)

Properties - Yellow needles, sol alcohol, HOAc, and benzene, insol water May be sub limed Its alkaline solution is red Its barium salt is easily soluble Gives purpurin on fusion with KOH Nitric acid oxidises it to phthalic Reduced by HI and P to a dihydride, which dyes alumina mordants like quercitron (Rosenstiehl, A Ch [5] 18, 224, C R 79, 764) Yields anthracene on distillation with zinc-dust

NH, Aq at 150° yields brown needles of $\mathbf{C}_{14}\mathbf{H}_{4}\mathbf{O}_{2}(\mathbf{OH})(\mathbf{NH}_{2})$ (Liebermann, A 183, 217)

Acetyl derivative C14H8O2(OAc)2 [1840] Di-methyl ether [180°] (Plath, B 9, 1204)

Di-ethyl ether $C_{14}H_6O_2(OEt)_2$ [170°].

(B 1, 4') Di-oxy-anthraquinone CH CH—C CO C C(OH) CH Anthrarufin. CH C(OH) C CO C CH—CH

Formed in small quantity (2g), to gether with anthraflavic acid (30 g) and m-'benzdioxyanthraquinone' (5 g), by the action of H₂SO, on m oxy benzoic acid (100 g) (Schunck a Romer, B 11, 1176, 161b) Formed Formed also by potash fusion from anthraquinone (ρ) disulphonic acid (Liebermann a Dehnst, B 12, 1287), and by the action of nitrous acid on the di amido anthraquinone Obtained by reduction of di nitro anthraquinone [above 300°] (Römer, B 16, 369)

Properties - Yellow tables, insol water, sl. sol alcohol, HOAc, ether, and CS., v sol benz-Forms oxyanthrarufin on fusion with KOH Almost insol baryta water, Na₂CO₂, and NH,Aq, sol KOHAq Its solution in H.SO, is cherry red with scarlet fluorescence Its Ca and Ba salts are crimson and insoluble

Acetyl derivative C₁₄H₆O₂(OAc)₂ [244°] Got by oxidising (β) di oxy anthracene with CrO,

Yellow needles ın HOAc

Di-oxy-anthraquinone C₁₄H₂O₄ Anthraflavic d [above 330°] S (95 p c alcohol) 1 18 at 10° (Rosenstiehl, Bl [2] 29, 401, 434) A by product in the preparation of alizarin, being formed by fusing anthraquinone (a)-disulphonic acid with KOH (Schunck, B 4, 360, 8, 1628, 9, 379, 679, Perkin, C J 24, 1109, 26, 19, 29, Formed also from m oxy benzoic acid 851) and H SO, (v supra) Radiating yellow needles (from alcohol), insol ether and benzene, sl sol HOAc Its solution in H SO, is yellow solution in alkalis is yellowish red Its Ba and Ca salts are sl sol water It does not dye mor-Potash fusion forms flavopur danted cotton purin Distillation with zinc dust forms anthra-Boiling with zinc-dust and NH3Aq forms cene $C_{14}H_{10}O_3$, whence $C_{14}H_{1}(OAc)_3$ [165°] (Lieber mann, B 21, 445)

Salts $-Na_2''$ 5aq sl sol water -BaA''xaq

reddish brown needles

C₁₄H₆O₂(OAc)₂ Di-acetyl derivative [229°]

Dibensoyl derivative C14H6O2(OBz)2 $[275^{\circ}]$

Di methyl ether C, H,O. (OMe)₂ [248°] Di-ethyl ether [232°] Yellow needles

Di-oxy anthraquinone C,4H,O, [above 330°] Isoanthraflavic acid Occurs in crude commercial alizarin, being formed by fusing anthra-quinone (3) disulphonic acid with potash potash (Schunck & Römer, B 9,379, 15, 1041, Perkin, C J 29, 851) Yellow needles (containing aq), almost insol benzene and ether, sl sol HOAc and alcohol It dissolves in cold baryta-water and in KOHAq with dark red colour Does not possess tinctorial properties. Its solution in H₂SO₄ is red. Yields anthrapurpurin on fusion H₂SO, 18 red

with KOH—BaA" raq red needles, v sol Aq
Di-acetyl derivative [o 195°] Crystals,
Di ethyl ether [194°] Yellow needles

(B. 1, 1' or 3')-Di-oxy-anthraquinone C₆H₈(OH) C₂O₂ C₆H₄OH. Chrysasın [192°]. Formed by eliminating amidogen from di oxytetra-amido-anthraquinone (hydrochrysamide) (Liebermann a Giesel, B 8, 1643, 9, 829, A 183, 184) Formed also by fusing anthraquinone χ disulphonic acid with potash (Liebermann a Dehnst, B 12, 1287) Golden laminæ or reddishbrown needles, m sol alcohol and HOAc. Insol. cold NH,Aq and Na,CO,Aq Its solution in KOHAq is yellowish red, and that in H,SO, Its solution is red Potash fusion yields oxychrysazin, and o- and m- oxy-benzoic acid Yields anthracene when distilled with red hot zinc dust Barytaand lime water give red pps Does not dye mordanted cotton

Dr-acetyl derivative [232°] Prepared by oxidising di-acetyl-chrysazol C₁₄H_a(OAc)₂ with CrO₂ (Liebermann, B 12, 186)

Di-oxy-anthraquinone C₁₄H₅O₄ Isochrysasın [175°-180°] Formed, together with m-benzdioxyanthraquinone,' by the action of nitrous acid and alcohol on the dye C_{2s}H₁₇N₃O₅ got from o di nitro anthraquinone and H₂SO₄ (Lifschütz, B 17, 897) Deep red needles (from alcohol), readily sublimed Its solutions in NH₂AQ and KOHAQ are violet red, that in H₂SO₄ is reddish-yellow Its Ba salt is insoluble It does not dye mordants

Dr-acetyl derivative [160°-165°] Needles

Di oxy-anthraquinone $C_{14}H_8O_4$ 'm-Bensdroxyanthraquinone' [298°] A product of the action of H_2SO_4 on m-oxy benzoic acid (Schunck a Römer, B 11, 969) Formed also as above Yellow needles, insol water and CS_2 , sol alcohol, HOAc, ether, and benzene Its alkaline solution is yellow Gives purpurin by potash-fusion Its solution in H_2SO_4 is brownish-yellow When freshly ppd it dissolves in hot baryta-water, and on cooling the Ba salt separates in red needles, which, after drying, are insoluble Has no tinctorial power

Di-acetyl derivative [199°] Needles Di-oxy-anthraquinone C₁₄H₈O₄ Frangulic acid [254°] Obtained, together with glucose, by hydrolysing frangulin which occurs in the bark of Rhamnus Frangula (Faust, A 165, 229) Orange needles (containing 1½aq), sl sol hot water, m sol alcohol Its solution in KOHAq is cherry red Its ammoniacal solution gives a red pp with BaCl₂ Distillation over zinc dust gives anthracene

Di-acetyl derivative [184°] Prisms
Di oxy anthraquinone

C₅H₄ CO C CH C(OH) . Hystazarın [282°] Formed by heating pyrocatechin (5 g) with phthalic anhydride (6 8 g) and H₂SO, (75 g) at 145° for 5 hours (Liebermann a Scholler, B 21, 2503, 22, 683) Orange yellow needles (from acetone), almost insol benzene, v sl sol alcohol, ether, and HOAc Its solution in KOHAq is blue, that in NH₂Aq is violet, and that in H₂SO₄ blood-red The Ba salt is blue, the Ca salt violet and insol water It dyes mordants slightly Yields anthracene on distillation with zinc-dust

Dr-acetyl derivative [207°]. Needles Ethyl ether C.H.O.(OH)(OEt). [284°-

240°] Yellow needles, forming a crimson solution in alkalis

D1-ethyl ether $C_1H_4O_2(OEt)_2$ [160°-163°]. From hystazarin, KOH, and Etl Yellow needles

Eleven di oxy anthraquinones have been described, but ten only are indicated by theory

Tri-oxy-anthraquinone

C_oH CO C C(OH) C(OH)

CO C C(OH) CH

Purpurn [253°]

Occurs in madder root, probably as glucoside (Colin a Robiquet, A Ch [2] 84, 244, Gaulthier de Claubry a Persoz, A Ch [2] 48, 69, 51, 110, Runge, A Ch [2] 63, 282, Schnel, A 60, 74, Debus, A 66, 351, 86, 117, Wolff a Strecker, A 75, 1, Rochleder, A 80, 321, 82, 205, Stenhouse, Pr 12, 633, 13, 145, Schutzenberger, J 1864, 542, Bl [2] 4, 12) Formed by the action of MnO₂ and H₂SO₂ at 150° on alizarin (De La lande, C R 79, 669) and on quinizarin (Baeyer a Caro, B 8, 152), and also by heating tri bromo-anthraquinone with H₂SO₄ at 200° (Diehl, B 11, 184) It may be separated from alizarin by repeatedly dissolving in boiling alum solution and ppg by acid Orange prisms containing aq (from dilute alcohol) or dark-red anhydrous needles (from absolute alcohol) May be sub SI sol boiling water, forming a yellow limed Its ethereal solution is yellow and shows lıquıd two absorption bands (Stokes, C J 12, 220, Vogel, B 9, 1641) Its solution in H2SO, is rose red and shows three absorption bands Aqueous KOH, Na₂CO₃, and NH₃ yield purple red solu-Almost insol alcoholic potash Barytawater forms an insoluble purple lake Its alka line solution is oxidised in daylight by the air becoming yellow (unlike alizarin) the product containing phthalic acid (Schunck a Romer, CJ 31, 665, Dralle, B 17, 376) Boiling alum forms a pink solution with yellow fluorescence Lead acetate gives in an alcoholic solution a darkcrimson pp, soluble in excess, forming a ciimson liquid with three absorption bands (the lead compound of alizarin is insol alcoholic lead acetate) Dyes cotton, mordanted with alumina,

Reactions —1 Yields anthracene on heating with sinc dust —2 Forms some quinizarin when heated in sealed tubes at 300°—3 Phosphorus and NaOHAq reduce it to purpuroxanthin —4 Nitric acid oxidises it to phthalic acid —5 Aqueous ammonia forms brown purpuramide $\mathbf{C_{14}H_3O_2(NH_2)(OH)_2}$

Acetyl derivative C₁₄H₂O₂(OAc)₃ [198°] (L), [200°] (S a R) Yellow needles

Ethylether C₁₄H₅O₂(OEt), Red crystals Tri oxy anthraquinone C₁₄H₅O₂(OH), Anthrapurpurm Isopurpurm [above 330°] A by product in the preparation of artificial alizarin, being formed by fusing anthraquinone (β) disulphonic with potash (Perkin, C J 25, 559, 26, 425, 29, 851, Caro, B 9, 682) Formed also by potash-fusion from isoanthrafiavic acid, from m benzdioxyanthraquinone (Schunck a Römer, B 9, 679, 11, 972), and from (a) di bromo anthraquinone (Perkin, C J 37, 557) Orange needles (from alcohol), v sol. hot alcohol, sl sol hot water and ether Conc H₅SO₄ forms a red solution, potash, NH₅Aq, and Na₂CO₂Aq give a violet solution. Sl. sol hot baryta-water, forming

a violet solution Alcoholic lead acetate gives a purple pp, sol excess It colours mordants

Reactions -1 Nitric acid gives no phthalic acid -2 Aqueous ammonia at 100° forms an unstable blue dye, decomposed by HCl or KOH with regeneration of anthrapurpurin -3 Aqueous ammonia at 170° forms anthrapurpuramide $C_{14}H_{2}O_{2}(OH)_{2}(NH_{2})$ which does not dye mordants (Perkin, C J 33, 216)

Tri-acetyl derivative [2229] Yellow scales

Tri-bensoyl derivative [185°] Crystals Mono ethyl ether $C_{1}H_{2}O_{2}(OH)_{2}(OEt)$ [265°] Orange red needles (Liebermann a Jellinek, B 21, 1170)

Dr-sthyl C₁₄H₅O₂(OH)(OEt)₂.

Tri-oxy-anthraquinone C14H2O, Flavopurpurm [above 330°] Formed by potash fusion from anthraflavic acid and from anthraquinone (a) disulphonic acid Purified by means of its lead salt (S a R , C , Liebermann, B 21, 441, 2524) Golden needles (from alcohol), v sol. cold alcohol Its solution in conc H2SO, is red, that in KOHAq is purple, becoming red on dilution Sl sol baryta water, forming a red solution Its solution in NH, Aq and Na2CO, Aq is yellowish red Alcoholic lead acetate forms a reddish brown pp, v sl sol excess On heating with phenyl cyanate at about 160° it forms C₁₄H₆O₃(O CO NHPh)₂ crystallising in yellowish plates (Tesmer, B 18, 2610)

Di-acetyl derivative [238°] plates

Tri acetyl derivative [196°] Yellow needles

Di-bensoyl derivative [210°] Needles Ethyl ether C14H,O2(OH)2(OEt)

Dr-ethyl ether [209°] Needles

Tri oxy anthraquinone

C.H. CO C C(OH) C(OH) Anthragallol [310°]

(Cahn, B 19, 2335) Formed by heating a mixture of benzoic acid, gallic acid, and H₂SO₄ at 70° (Seuberlich, B 10, 38) Formed also from pyrogallol, phthalic anhydride, and H2SO, Orange needles (by sublimation), nearly insol water Its alkaline solution is green HNO_s forms phthalic acid Distillation over zinc dust gives anthracene Dyes alumina mordants brown Alcoholic lead acetate ppts violet brown C14H3O3Pb2OAc Boiling alcoholic NH, forms anthragallolamide C14H,O2(NH2)(OH)2 crystallising in black needles with green reflex HCl and HOAc form C14H10O4 whence C14H2AC4O4 [205°] (L)

Needles Tri-acetyl derivative [173°] Ethyl ether C₁₄H₂O₂(OH)₂OÉt [175°] From the K salt and Etl at 80° The Pb salt and EtI at 220° yields an isomeride [245°]

Dr-ethyl ether [184°] Formed from the K salt (L a. J) The Pb salt yields an isomeride

[198°]

Tri-oxy anthraquinone C, H,O, Oxychrys-Formed by potash-fusion from chrysazin and from anthraquinone ρ and χ disulphonic acids (Liebermann, A 183, 191, 12, 1289). Probably identical with oxyanthrarufin Red needles (from alcohol). Its alkaline solutions are blue.

Baryta-water gives a blue insoluble pp Dyes mordants

Tri-acetyl derivative [193°] Yellow needles

Tra-oxy-anthraquinone

C₆H₂(OH) C₂O₂.C₆H₂(OH)₂. Oxyanthrarufin. Prepared by fusing anthrarufin with KOH (Liebermann a Boeck, B 11, 1617) Red needles (by sublimation) Its alkaline solutions are blue. Dyes mordants like alizarın

Tetra-oxy anthraquinone C14H6O6 \$.6.

C(OH) CH C CO C CH = C(OH) Anthrachrys-one Mol w 272 Formed by heating s di-oxybenzoic acid alone or with H2SO4 (Barth a Senhofer, A 164, 109, Noah, B 19, 754) needles (containing 2aq), not melted at 360° sol alcohol, v sl sol water and ether Yields anthracene on distilling with zinc-dust Its solution in KOHAq is reddish - yellow -Ba(C14H,O6)2 11aq red needles

Tetra-acetyl derivative [253°] Needles. Tetra-oxy-anthraquinone C14H6O6 Oxypur-Formed by heating purpurin with KOH at 240° (Diehl, B 11, 185) Brown nodules, not Almost msol alcohol Its melted at 290° alkaline solution is brownish red. Its acetyl derivative melts above 240°

Tetra-oxy-anthraquinone

CH C(OH) C CO C C(OH) C(OH)
CH C(OH) C CO C CH—CH
[above 275°] Obtained by heating its di-methyl ether with HOAc and HCl at 200° Formed also by heating alizarin with H2SO, at 210° (Graebe, B 23, 3739) Long red needles, sol HOAc, sl. sol alcohol Dyes mordants well Its solution in H₂SO₄ is blue The Ba and Ca salts are insol. water Yields anthracene on distillation with zınc dust

Tetra-acetyl derivative [201°] Needles. Di-methyl ethyl [225°-230°] Obtained D:-methyl ethyl [225°-230°] by heating hemipic acid $C_6H_2(OMe)_2(CO_2H)_2$ [6 5 2 1] with hydroquinone and H_2SO_4 at 130 (Liebermann a Wense, B 20, 864, A 240, 298) Minute brownish red plates Forms a bluish-violet solution in alkalis and a blue solution in H2SO, Does not dye. Yields C14H4O2(OMe)2(OAc)2 [211°

Tetra-oxy-anthraquinone C, H,O, Ruft-Formed by heating opianic acid with H2SO at 180° (Liebermann a Chojnacki, B 4, 194, A 162, 322) Yellowish red needles, sl. sol boiling water, m sol hot alcohol Its solution in KOHAq is violet red, that in NH,Aq is reddish-brown, and is ppd by BaCl, and CaCl. Yields anthracene on distilling with zinc dust. Conc H2SO, gives a violet red solution Dyes alumina mordants brownish red -BaC14HeOe aq.

Tetra-oxy-anthraquinone C₁₄H₂O₆ (a)-Oxy-thragallol [above 350°] Formed, together anthragallol [above 350°] with the (8)-isomeride and rufigallic acid, by heating pyrogallol with m-oxy-benzoic acid and H₂SO₄ at 150° (Noah, Liebermann a. Kostanecki, 4 240, 270) Golden needles (from alcohol) or red needles (from benzene) Conc. H₂SO₄ forms a violet solution KOHAq gives a green solution Insol baryta-water mordants

Tetra-acetyl derivative [209°].
Tetra-acy-anthraquinone C₁₄H₂O₄ (3)-Oxy-anthragallol. [above 880°] Formed as above. x x 2

Red needles (from alcohol), insol benzene. Cone H₂SO₄ gives a brownish yellow solution KOHAq forms a green solution Dyes mor-

Tetra-acetyl derivative [189°]

Of the two oxyanthragallols one should have the hydroxyls in the position 1,2,3,2', and the other in 1,2,3,4'

Penta-oxy-anthraquinone C(OH) CH C CO C CH = C(OH)Formed by CH C(OH) C CO C C(OH) C(OH) heating gallic acid with s-di oxy benzoic acid H₂SO₄ for 15 minutes at 165° (Liebermann a Noah, B 19,751, A 240,273) Small yellowishred plates (by sublimation), not melted at 360° V sol hot alcohol, sl sol ether, nearly insol. benzene and hot water Its solution in KOHAq is green, that in H2SO4 is brownish red Dyes

[229°] Penta-acetyl derivative Needles

Hexa oxy-anthraquinone

mordanted fabrics

 $\mathbf{C}(\mathbf{OH}) \mathbf{C}(\mathbf{OH}) \mathbf{C} \mathbf{CO} \mathbf{C} \mathbf{CH} = \mathbf{C}(\mathbf{OH})$ O(OH) = OH C CO C C(OH) (C(OH) Ruffgallic acid Formed by heating gallic acid with H₂SO₄ (Robiquet, A 19, 204, Wagner, C C 1861, 47, Löwe, J pr 107, 296, Jaffé, B 3, 694, Widman, B 9,856, Klobulowskia Nölting, B 9,856, Klobulowskia Nolting, B 9, RufigallicB 8, 819, 9, 1256, 10, 880) Red orystals (containing 2aq), v sl sol alcohol and ether Its solution in cone KOHAq is blue, becoming violet red on dilution Conc H2SO, forms a red solution Baryta-water forms a blue insoluble Dyes fabrics, mordanted with alumina, salt brown, with iron salts, black

Reactions -1 Yields anthracene on heating with sinc-dust -2 Nitric acid gives no phthalic acid—3 Boiling HIAq and P form minute needles of $C_{14}H_{10}O_{7}$ —4 Potash-fusion yields m-oxy benzoic acid, γ -oxy-isophthalic acid, and an anhydride of hexa-oxy-diphenyl C₂₂H₁₈O₁₁ 4aq, crystallising in colourless needles (Malin, A 141, 346, Schreder, M 1, 432)

Hexa-acetyl derivative Needles Chloro-acetyl derivative C18H2ClOgo Needles

Tra-ethyl ether [195°] Orange needles Tetra-methyl ether [c 220°] Needles Tetra-ethyl ether [above 180°] needles

Hexa-ethyl ether C,H,O (OEt), 140°] Orange needles, sol hot alcohol

References — Bromo, Chloro-, and Nitro-oxyanthraquinone and Oxyamido anthraquin-

OXY-ANTHRAQUINONE CARBOXYLIC

ACID C₆H₄<00>C₆H₂(OH)CO₂H [260°]. Prepared by fusing anthraquinone carboxylic acid with caustic soda (Hammerschlag, B 11, 83) Orange needles (by sublimation) Yields phthalic acid on oxidation with HNO, Ba salt is a blue pp Its alkaline solutions are purple

(erythro)-Oxy-anthraquinone-carboxylic acid [238°] Formed by heating (erythro)-oxy-methylanthraquinone with H₂SO₄, a portion of the quinone probably oxidising the methyl of the rest (Birukoff, B 20, 2488) Long yellow needles V sol boiling water Heated to about

quinone. The Ca and Ba salts are sparingly soluble

Di oxy-anthraquinone carboxylic acid C.H.(OH), C.O. C.H.CO.H Alexarn carboxylic acid [806°] Formed by soda-fusion from the sulphonic acid got by heating anthraquinope carboxylic acid with H2SO4 (Hammerschlag, B 11, 86) Dull-red powder or red needles (by sublimation), v sol aqueous NaOAc Decomposed by heat into CO₂ and alizarin Its alka line solutions are purple Gives a red lake with alumina Nitric acid oxidises it to trimellitic $acid -Ba_3(C_{15}H_5O_6)_2$ blue pp

Di oxy-anthraquinone carboxylic acid C_{1.}H₂O₄ Munjistin Purpuroxumina (231°) Occurs in madder (Schunck a Römer, 231°) Occurs in madder (Schunck a Römer, 231°) Age (131°) Age (B 10, 172, C J 31, 666, 33, 422) and in mun jeet or East Indian madder (Stenhouse, Pr 12, 633, 13, 86, 145) Golden scales (from HOAc), split up at 233° into CO₂ and purpuroxanthin M sol boiling water and alcohol Its alkaline solutions are red Conc H₂SO₄ forms an orange Dilute nitric acid oxidises it to solution phthalic acid Fuming HNO, gives a di nitroderivative Dyes fabrics, mordanted with alu mina, orange, with iron mordants, brownish red Forms a red insoluble Ba salt purpurin when boiled for a long time with conc KOĤAq Ammonia at 100° forms purpurin amide Br in HOAc forms di bromo-purpuroxanthin [231°]

Tri-oxy-anthraquinone carboxylic acid C15H8O, Purpurin carboxylic acid Pseudopurpurn [220] Occurs in madder (Schutzen berger a Schiffert, Bl 4, 13, Rosenstiehl, C R 84, 561, Liebermann, B 10, 1618) Red plates, almost insol water and alcohol Split up by heat, or by boiling with water, potash, or alco hol into CO2 and purpurin Its alkaline solution is orange-red Does not dye mordanted fabrics unless the water is free from CaCO, (difference Bromine water yields bromo from purpurin) purpurin [275]

O OXY-ANTHRAQUINONE SULPHONIC ACID C₆H₄ C₂O C₆H₂(OH)(SO₈H) [1 6 2 3 or 4] Erythro oxy anthraquinone sulphonic acid Formed from o amido anthraquinone sulphonic acid by the action of nitrous acid (Lifschutz, B 17, 900) Yellow plates, v sol water, alcohol, and ether Its alkaline solution is red On fusion with potash it gives alizarin -AgA' needles

Anhydride $C_{14}H_6O_2 < {0 \atop SO} > 0$ needles, insol water, alcohol, and ether, sl sol HOAc Requires to be heated with alkalis before yielding the acid

Oxy anthraquinone sulphonic acid Formed by sulphonating erythro oxy anthraquinone at 130° Sol water and alcohol, insol ether Its alkaline solution is reddish yellow Baryta gives a blood red pp, crystallising from hot water BaCl₂ gives a similar yellow pp Lead acetate gives a yellowish-brown pp, sol hot water Gives neither alizarin nor purpurin on potash

m-Oxy-anthraquinone sulphonic acid $C_{14}H_{2}O_{2}(OH)(SO_{2}H)$ Formed by heating *m*-oxyanthraquinone with $H_{2}SO_{4}$ at 120° (Von Perger, needles V sol boiling water Heated to about J pr [2] 18, 178) Crystals (from alcohol), m. 270° it loses CO₂, and gives (erythro)-oxy-anthrasol cold water, insol ether Its alkaline solu-

tion is reddish brown Lead acetate gives a brownish yellow, and lime-water a brown, pp Yields alizarin sulphonic acid on fusion with potash at 180°—BaC₁₄H₅SO₅ orange crystals When (a)- or (β)- anthraquinone disulphonic

acid is fused with moist potash, a mixture of an thraquinone disulphonic acid, oxyanthraquinone sulphonic acid, and tri oxy-anthraquinone is got The mono sulphonic acid is obtained by stopping the fusion as soon as the blue colour begins to turn violet (Graebe a Liebermann, 4 160, 139) According to Von Perger (J pr [2] 18, 168) it is doubtful whether the product is not a di oxyanthraminone sulphonic acid The acid prepared from (a)-anthraquinone disulphonic acid gives on fusion with potash anthraflavic acid and flavo-purpurin, and is therefore isomeric with that from (B) anthraquinone disulphonic acid, which gives isoanthraflavic acid and anthra purpurin on potash fusion

Di-oxy anthraquinone sulphonic acids

C₁₄H₅O₂(OH)₂(SO₃H) Pure alizarin heated with strong H₂SO₄ at 120° forms at least three sul phonic acids On adding water two sulphonic acids dissolve and another remains on the filter as a brown mass The latter dissolves in alka lis, forming a cherry red liquid It is slightly soluble in water, but is slowly decomposed by boiling water, regenerating alizarin Of the two sulphonic acids which are readily soluble, the one that is formed in greatest quantity is the most soluble, and it is decomposed by potash fusion at 200° without forming either alizarin or purpurin The other sulphonic acid is formed in very small quantity, but by potash fusion it is converted at 140° into purpurin, the mass becoming crimson (Von Perger, J pr [2] 18,

D1-oxy-anthraquinone sulphenic acid ₁₄H₅O₂(OH)₂SO₃H Quinizarin sulphonic acid Formed in small quantity in the preparation of quinizarin from hydroquinone, phthalic anhydride, and H₂SO₄ (Liebermann, A 212, 11) Its Na salt forms a deep orange solution, turned deep blue by alkalis It does not dye mor-

OXY-AZELAIC ACID $C_7H_{13}(OH)(CO_2H)_{22}$ [91°] Formed by the action of NaOHAq upon the product of the action of Br and a little red P upon azelaic acid (Bujard a Hell, B 22, 68) Nodules (from water or ether) — BaA" aq S
2 56 at 18° — CaA" 1aq S 65 at 20° —
ZnA" 2aq S 623 at 20° — SrA" 1aq — MgA" 2aq — CdA" 2aq — CuA' 1 aq — PbA" aq $-Ag_2A''$

OXY-AZO- compounds v Azo- compounds

OXY-AZOPHENÎNE C,H,,N,O Formed by heating nitroso m-oxy-diphenylamine with aniline and aniline hydrochloride on the water bath (O Fischer a. Hepp, B 20, 2481, Kohler, B 21, 910) Needles (from toluene), sol alcoholic NaOH, insol NaOHAq Conc. H2SO, forms a reddish-brown solution.

DI-OXY-BEHENIC ACID C₁₁H₄₂(OH)₂O₄.
[127°] (H), [183°] (H a G) Formed by boaling oxy-erucic acid with potash (Haussknecht, A 143, 53), or by oxidising erucic acid with alkaline KMnO₄ (Irwantzoff, J R 21, 13, J pr 39, 884; Hasura a. Grüssner, M 9, 947) Plates from alcohol), insol water and ether PL at gives iodobehenic acid reduced by sinc and

HCl to behenic acid NaA' grains, sl. sol. water -BaA'2 insoluble pp

Iso-di oxy-behenic acid C22H42(OH)2O2 [99°]. Formed by oxidising brassic acid with alkaline KMnO₄ (Grüssner a Hazura, M 10, 197) Minute plates, insol water and ligroin, v sol hot alco-

DI-OXY-BEHENOLIC ACID C22H404 Formed by oxidising behenolic (benolic) acid with fuming HNO, (Haussknecht, A 143, 46) Yellowish scales (from alcohol) —AgA' white pp

OXYBENZALDEHYDE v OXYBENZOIC ALDE HYDE

OXYBENZAMIDE v Amide of OXYBENZOIG

Ethylo-OXY-BENZAMIDINE C₆H₄(OEt) C(NH) NH₂ A product of the action of alcoholic HCl, followed by alcoholic NH, on C₆H₄(OEt) CN (Pinner, B 23, 2952) The hydrochloride B'HCl [218°] crystallises in short hexagonal columns, v sol water

Ethyl ethyl p Oxy benzamidine hydrochloride C₆H₄(OEt) C(NH)NH₂Cl [260°] is formed by the action of alcoholic NH, on the hydrochloride of ethyl p oxy benzimido-ether It is converted by acetoacetic ether and NaOHAq into ethylated dioxy phenyl methyl pyrimidine

C₆H₄(OEt)C N CMe

OXY-BENZENE v PHENOL

Di-oxy-benzene v Hydroquinone, Pyrocate-CHIN, and RESORCIN

u-Tri-oxy-benzene C₆H₃(OH), [1 2 4] Oxy hydroquinone [140 5°] Formed, together with hexa oxy diphenyl, by fusing hydroquinone (1 pt) with moist NaOH (9 pts) (Barth a Schreder, M 4, 176, 5, 589) Monoclinic plates (from ether), V e sol water, $abc = 751101, \beta = 91^{\circ}46'$ alcohol, ether, and HOAc, almost insol chloroform and benzene Its alkaline solution rapidly becomes brown through absorption of oxygen FeCl, gives a transient bluish green colour H₂SO, forms a green solution becoming cherryred on warming Bromine forms C₆Br₈(OH)O₂
[206°] Nitric acid yields greyish blue crystals of oxyquinhydrone

Tri-acetyl derivative C.H. (OAc). [96°] C.H.(OMe)(OH), [2 4.1]. Methyl ether [84°] Got by reducing the methyl ether of oxyquinone with aqueous SO₂ (Will, B 21, 606) Colourless plates Turned yellow by FeCl, being reconverted into CH₂(OMe)O₂.

Tri-methyl ether C.H.; (OMe). (247°). Formed from the preceding ether, methyl iodide, and KOH (W) Obtained also from assrone C.H.(OMe), CH CHMe by oxidation to C.H. (OMe) CO.H and distillation of this acid with lime (Rizza a Butlerow, J R 1887, 1). Oil, volatile with steam

Mono-ethyl ether C.H. (OH)2(OEt)[1 4 8] [112°]. Formed by reduction of the ethyl ether of oxy-quinone C.H. (OEt)O2 with SO2. Colourless prisms Sublimes in fine plates water, alcohol, and ether, m sol benzene Fe₂Cl_e gives a dark brown colouration.

Tra-sthyl ether CaHs(OEt), Formed by ethylation of the preceding body. Long white glistening needles, v e sol. alcohol and ether, insol water, volatile with steam. This body is identical with that obtained from esculetin, which is therefore a derivative of s-tri-oxy-benzene (Will a Pukall, B. 20, 1133, Herzig a Zeisel, M 10, 150)

Isomerides are described as Philosoglucia

and Pyrogattot.

s-Tetra-oxy-benzene C₂H₂(OH)₄ [1 2 4 5] [c 218°]. Formed by reducing di oxy-quinone with SnCl₂ (Nietzki, B 21, 2377) Colourless plates, v e sol water, alcohol, and ether Its aqueous solution rapidly turns brown, and its alkaline solution is oxidised by air or by FeCl₂ to di oxy-quinone

Acetyl derivative CaH2(OAc), [217°]

Colourless plates

Di-methyl ether

C_cH₁(OH)₂(OMe)₂ [1 4 2 5] [166°] Formed by reducing C_cH₂O₂(OMe)₂ with stannous chloride (Nietzki a Rechberg, B 23, 1217) Colourless plates

Di-ethyl ether C₆H₂(OH)₂(OEt)₂[1 4 2 5] [188°] Got in like manner Colourless needles (from hot water) Yields C₆H₂O₂(OEt)₂ on oxidation Acetic anhydride forms the compound C.H.(OAc)₂(OEf)₃ [148°]

C₆H₂(OA₆)₂(OE₅)₂ [148°]

Tetra-ethyl ether C₆H₂(OE₅)₄ [143°]

Formed from C₆H₂(OH)₂(OE₅)₄ alcoholic NaOEt and EtBr at 100° (Nietzki, B 23, 1214)

Colourless plates, smelling like anise May be

sublimed

u-Tetra-oxy-benzene De-methyl ether $C_8H_3(OH)_2(OMe)_2$ [1 4 3 5] [158°] Formed by reducing the corresponding $C_8H_1O_2(OMe)_2$ with SnCl₂, or with SO₂ (Hofmann, B 8, 67, 11, 332, Will, B 21, 609) Needles, reconverted into the quinone by FeCl₂ HOAc forms an acetyl derivative [133°] which forms a green solution in H_2SO_4 Ac₂O forms an acetyl derivative [128°] which does not give a green solution in H_2SO_4 (H) Benzoyl chloride yields $C_8H_2(OMe)_2(OBz)_2$ [245°], v sl. sol alcohol

Tre-methyl ether C₂H₂(OH)(OMe)₂ [146°] Formed, together with the tetra-methyl ether by the action of methyl include and KOH on the di-methyl ether Needles (from alcohol)

Tetra-methyl ether C_eH₂(OMe)₄ [47°]. (271°). Plates (from ether) Yields C_eBr₂(OMe)₄

17207

c-Tetra-oxy-benzene D1-methyl ether C_H_(OH)_1(OMe)_. D1-methyl apronol [106°] (298°). Formed by heating aprolic acid C,H_O_0(OMe)_cO_1H with alcoholic potash, at 180° (Ciamician a Silber, B 22, 119, 2482, 23, 2291) Insol water, sol alcohol, ether, and benzene. Its solution in KOHAq becomes brownish-red Ferric chloride gives a violetblack colour Lead acetate gives a gelatinous pp AgNO, forms minute needles, quickly turning black Yields a crystalline acetyl derivative [144°]

Tetra-methyl ether C.H.2(OMe), [1 2 3 4]

[81°] White needles, v sol ether

Hexa-exy-benzene C₄(OH)₄ (so-called 'tri-hydrocarboxylic acid' of Lerch) Long nearly colourless needles. Soluble in hot water, slightly soluble in cold water, alcohol, ether, and benzene.

Formation —1 By the action of dilute HCl apon freshly prepared carbonic-oxide potassium. 2 By reduction of tri-quinone C₆O₆ with stannous shloride.

Properties —Reduces AgNO₂ in the cold. Is oxidised by HNO₂ to benzené-tri-quinone Gives a violet colouration with Fe₂Cl₂. The solution in aqueous Na₂CO₂ is readily oxidised by the air to tetra oxy-quinone C₆(OH)₄O₂. By distillation with zinc dust it gives benzene and diphenyl By evaporation in an open dish with dilute KOH it yields croconic acid C₁H₂O₄.

it yields croconic acid $\tilde{C}_1H_2O_5$ Salt $C_6(OK)_6$ Formed by combination of CO with K at 80°, occurring as a by product in the preparation of K (Liebig, A 11, 182, Brodie, A 113, 358, Lerch, A 124, 20) Grey mass,

becoming explosive on exposure to air

Hexa-acetyl derivative C₄(OAc),
[203°], small colourless prisms, sl sol hot

acetic acid, nearly insol alcohol, ether, and benzene (Nietzki a Benckiser, B 18, 505, 1833)

OXY-BENZENE CARBOXYLIC ACID v OXY BENZOIC ACID

Oxy-bensene dicarboxylic acid v Oxy PHTHALIC, Oxy-ISOPHTHALIC, and Oxy TEREPH THALIC ACIDS

Tri-oxy-bensene carboxylic acid v Gallic acid

Tri-oxy-benzene tri-carboxylic acid v
Philoroglucin tricarboxylic acid

Di-oxy benzene tetra-carboxylic acid v Hydroquinone tetra-carboxylic acid

DI OXY-BENZENE-DIQUINONE v DI OXY DIQUINONE

OXY-BENZENE SULPHONIC ACID v
PHENOL SULPHONIC ACID

Di-oxy-benzene sulphonic acid C_sH₂(OH)₂SO₂H [280°] Formed by heating phenol 'β'-disulphonic acid with potash at 240° (Senhofer, J 1879, 749) Crystallises from water in needles (containing aq) Coloured violet by FeCl₂ — BaA'₂7aq — ZnA'₂27aq — PbA'₂8aq long thin plates

Isomerides Hydroquinone, Pyrocatechin,

and Resorcin sulphonic acids

OXY-BENZENYL-AMIDO-PHENYL MER CAPTAN $C_{15}H_{5}NSO$ s.e $C_{6}H_{4} \stackrel{N}{<} C_{6}H_{4}$ OH [129°] Formed by heating salicylic aldehyde with o-amido phenyl mercaptan (Hofmann, B 13,1237) Needles —B'HCl —Platinochloride B'₂H₄PtCl₄ pp

O-OXY-BENZENYL-AMIDOXIM

C₂H₄(OH) C(NOH) NH₂ Salacenyl amadoxim [99°] Formed from C₄H₄(OH) CS NH₂, hy droxylamine hydrochloride, and Na₂CO₂Aq (Spilker, B 22, 2774) Colourless needles, v sol alcohol and ether, m sol hot water Gives a greenish pp with CuSO₄ and a mirror with AgNO₃

Reactions —1 Ac.O forms the acetyl derivative and, on further digestion, the azoxim $C_eH_4(OH)$ C < N O OMe [77°] which yields an acetyl derivative [74°] —2 Concentrated sulphuric acid at 150° yields the sulphonic acid $C_eH_4(SO_eH)(OH)$ $C(NOH)NH_1$, v sl sol cold water, insol alcohol — 3 $C(CO_eEt$ yields $C_eH_4(OH)$ $C(NH_2)$ NO CO_eEt [96°] (Miller, B 22, 2799) —4 Succimo anhydride forms, on melting, the azoxim $C_eH_4(OH)$ $C(N_2OH)$ $CO_eH_4(OH)$ $CO_eH_4(OH)$

Phenyl cyanate forms by direct combination |

C.H.(OH) C(NOH) NH CO NHPh [119°]
Salts—B'HCl [175°] V e sol water—
B'2H.PtCl. —Na,C.H.N.O.—NaC,H.N.O.
Acetyl dervative

C,H4(OH) C(NOAc) NH2. [117°] White plates, si sol water

Di acetyl derivative Formed from the Na salt and AcCl Crystalline

Bensoyl derivative [173°] C₆H₄(OH) Č(NOBz) NH₂ Needles, v. sol ether Yields C.H. (OH) C.N.O. CPh [128°],

which forms a benzoyl derivative [120°]

Di-benzoyl derivative

C₆H₄(OBz) C(NOBz) NH₂ [127°] Formed from the amidoxim, NaOEt, and BzCl in ether distinct crystals

Ethyl ether C₆H₄(OH) C(NOEt) NH₂. (278°) Formed from the amidoxim, alcoholic NaOEt, and Etl Oil By HCl and NaNO2 it is converted into C₆H₄(OH) C(NOEt)Cl (234°)

Methyl derivative C.H. (OMe) C(NOH)NH2. [123°] Formed from C.H. (OMe) CN and alcoholic hydroxylamine Needles (from hot water) (Mıller, B 22, 2791) Yields B'HCl [168°] With AcoO it yields $C_{\bullet}H_{\bullet}(OMe)$ $C \leqslant \stackrel{N}{N} \supset CMe$ [68°] Aldehyde forms

 $C_8H_4(OMe) C < NH > CHMe [127 5°] CICO_2Et$ forms C₈H₄(OMe) C(NH₂) NO CO₂Et[120°], which on heating becomes C.H.(OMe) C.N.H.

Methyl-acetyl derivative

C₆H₄(OMe) C(NOAc)NH₂ [106°] Formed from the oxim and AcCl in chloroform Prisms

Methyl-benzoyl derivative $C_{*}H_{*}(OMe) C(NOBz)NH_{2}$ [148°] White granules, v sol alcohol

Methyl-ethyl derivative C_sH₄(OMe) C(NOEt) NH₂ [52°] Prisms, v sol. alcohol

Di ethyl derivative

C_eH₄(OEt) Č(NOEt) NH₂ (195° at 160 mm) Formed from the amidoxim, NaOEt, EtI, and alcohol Oil, miscible with alcohol and ether m Oxy benzenyl amidoxim

C_eH₄(OH) C(NH₂)(NOH) [71°] Made by heat ing m oxy-benzonitrile with hydroxylamine hydrochloride and Na₂CO₃ (Clemm, B 24, 829) Groups of needles, v sol water

Di-benzoyl derivative

[152 5°] Crystals C₄H₄(OBz) C(NH₂) NOBz Acetyl derivative

CaH4(OH) C(NH2) NOA0 [90°]

Drethyl ether C.H. (OEt) C(NH2) NOEt p-Oxy benzenyl-amidoxim Needles [158°] Made in like manner (Krone, B 24, 884—B'HCl [179°]

Acetyl derivative [122 5°] Bensoyl derivative [166°] [186°] Di-bensoyl derivative

Diethylether [84°] U-OXY-BENZENYL-O-PHENYLENE-DI-

AMINE C.H. < NH > C C.H.OH [228°] Formed by reducing the o nitro-anilide of salicylic acid with tin and HCl (Hübner a Mensching, B 18, 463; A 210, 345) Needles, v. sol. alcohol and

ether — B'HCl aq — B', H, SO, 4aq sparingly soluble needles

o-OXY-BENZENYL-DI-UREA C.H,2N4O, 2 & C_eH₄(OH) CH(NH CO NH₂)₂ Formed from sallcylic aldehyde and aqueous urea (Schiff, A 151, 199) Nodular groups of needles (containing aq) V sl sol water, sl sol alcohol, insol ether - $Cu(C_0H_{11}N_4O_2)_2$ Green pp Ethyl ether $C_0H_4(OEt)$ $CH(N_2H_2CO)_2$ aq

Crystals

By fusing salicylic aldehyde with urea there 18 formed (C,H,(OH) CH),(N,H,CO) p-Oxy-bensenyl-di-urea Methyl

C₆H₄(OMe) CH(NH.CO NH₂)₂ Formed anisic aldehyde, an aqueous solution of urea, and a little HOAc Yellow plates

DI-OXY-BENZIL Di-methyl derivative C_sH₄(OMe) CO CO C_cH₄(OMe) Anisil [133°] Formed by oxidising anisoin with alkaline copper solution (Boesler, B 14, 327) Golden needles (from alcohol)

Hexa-oxy-benzil Hexa-methyl derivative C₆H₂(OMe), CO CO C₆H₂(OMe), [189°] Formed by the action of sodium amalgam on an alcoholic solution of the tri methyl derivative of the amide of gallic acid (Marx, A 263, 253) Sating needles, coloured bluish green by H2SO.

p OXY-BENZIMIDO-ETHER Ethyl derivative C_eH₄(OEt)C(NH)(OEt) The hydro chloride is crystalline and is formed from C.H.(OEt)CN and alcoholic HCl (Pinner, B

23, 2953

C,HO, o-OXY-BENZOIC ACID C₄H₄(OH) CO₂H Saheyhe acad Mol w 138 [156°] (Hubner, A 162, 74), [159° cor] (Ressert, B 23, 2244), [157° cor] (Dunstan a Bloch sets, D 23, 2224), [16'7 cor] (Dunstan a Blooh, Ph [3] 21, 429) S 09 at 0° (Ost, J pr [2] 17, 230), 15 at 0°, 225 at 15°, 7 925 at 100° (Bourgoin, J Pharm Chim [4] 30, 488, C R 87, 62), H C 734,990 (Berthelot a Recoura, J Chiman, J pr [2] 40, 129) H F 106,000 (Von Rechenberg), 135,500 (S) Occurs in the blossoms of the meadow sweet (Sparca ulmosca) (Living a property of the courage of the coura meadow sweet (Spirza ulmaria) (Löwig a. Weidmann, P 46, 83), and in the leaves and stems of Tulipa, Yucca, and Hyacinthus (Grifiths, C J Proc 5, 122) Occurs as methyl ether in the oil of wintergreen (from Gaultheria procumbens) (Cahours, A 48, 60, Hartley, C J 53, 664) Methyl salicylate constitutes the essential oils of Gaultheria punctata and G leuco carpa (Köhler, B 12, 246)

Formation -1 By oxidation of o-oxy-benzyl alcohol (saligenin), and of o-oxy benzoic aldehyde (salicylic aldehyde) —2 By potash-fusion from salicin, coumarin, indigo, o-cresol (Barth, A 154, 360), toluene o-sulphonic acid, p-chlorotoluene sulphonic acid (Vogt, Z [2] 5, 577), and other bodies —3 By heating cupric benzoate with water in sealed tubes for 3 hours at 180° (Smith, Am 2, 338), of Ettling, A 53, 88) -From o-amido-benzoic acid by the diazoreaction (Hubner a Petermann, A 149, 129, cf derland, A 86, 147)—5 Together with p-oxy benzoic acid by heating phenol with COl, and alcoholic potash (Tiemann a Reimer, B 9, 1285)—6 By oxidising o-tolyl sulphure acid C.H., MeO SO, H with alkaline KMnO (Haymann a. Königs, B 19, 706) —7 By heating C.H.ONa with sodium carbonate in a current of carbonic oxide at 200° PhONa + Na₂CO₂ + CO

 $= C_2H_4(ONa) CO_2Na + HCO_2Na$ (Schroeder, A 221, 41) -8 By oxidising toluene o-phosphonic acid with alkaline KMnO₄ (Heymann a Königs, B 19, 3306)—9 By distilling sodium phenyl carbonate with NaOEt in a current of CO₂ (Hentschel, J pr [2] 27, 39) —10 By heating phenyl ethyl carbonate with NaOPh at 200° in a current of hydrogen, PhOEt being also formed 11. Together with PhOEt by heating Ph₂CO₃ with NaOEt in a current of hydrogen (H)

Preparation —By passing CO₂ over sodium-phenol heated at 180° C₆H₄(ONa)CO₂Na being formed and phenol distilling over (Kolbe, A 115, 201, J pr [2] 10, 93) CO2 is first absorbed, and this can also take place at a lower temperature, and the resulting sodium phenyl carbonate C.H.O CO.Na changes into the isomeric sodium salicylate C.H. (OH) CO.Na This change can take place at 130° The sodium salicylate reacts upon excess of sodium phenol at 180°, setting free phenol, which distils over, leaving basic so dium salicylate behind C.H. (OH) CO.Na + PhONa = PhOH + C.H. (ONa) CO.Na (R. Schmitt, J. pr. [2] 31, 404, cf. Baumann, B. 11, 1910) Salicylic acid is set free by acidifying the basic sodium salicylate By using a measured quantity of CO, starting the operation at a low temperature and finishing it at 130°, the formation of basic sodium salicylate may be avoided, so that half the phenol may be saved

Properties - Colourless needles (from hot water) or monoclinic prisms (from alcohol) Sublimes at 200° Volatile with steam FeCl. colours its aqueous solution violet, the colour not being removed by acetic acid Prevents ppn With of copper sulphate (2 mol) by alkalis albuminoids it forms compounds containing about 14 pc of the acid (Farsky, C C 1877, 148) Bromine-water yields a pp of C.H.Br.O in dilute aqueous solutions Iodine and potash give a red powder C_cH_sI(OI)CO₂K (Messinger a Vortmann, B 22, 2321) Antiseptic Anti-

rheumatic

Reactions -1 Split up into CO2 and phenol when rapidly heated to $2\overline{20}^{\circ}$, at $2\overline{50}^{\circ}$ diphenylene-ketone oxide [174] is formed (Klepl, J pr[2] 28, 217) Conc HClAq at 150° decomposes it in like manner (Graebe, A 139, 143) fusion also gives phenol—2 KMnO₄ oxidises it to formic acid and CO₂. Chromic acid micture acts in like manner—3 Chlorine forms chlorooxy-benzoic and di-chloro-oxybenzoic acids -4 Iodine and HIO, give mono, di-, and tri-, 10do-oxy benzoic acids and tri-10do-phenol -5 Nitrous acid passed into its ethereal solution forms nitro- and diazo oxy-benzoic acids (Goldberg, J pr [2] 19, 368) — 6 PCl, forms C₂H₄(COCl) O.POCl₂ (168° at 11 mm) This compound is partially decomposed on distillation, yielding o-chloro-benzoyl chloride Moist air converts it into C₆H₄(CO₂H) O PO(OH)₂ Further treatment with POl₅ at 170° forms C₈H₄(COOl) OPCl₄ (179° at 11 mm) converted by water into C₈H₄(CO₂H).OP(OH)₄ Excess of PCl₅ forms C₈H₄Cl CCl₅ (Couper, A 109, 370, Anschütz, A 228, 314, 239, 314, Chasanovitch, B 20, 1166) —7 PCl₅ forms C₇H₆ClPO₅, which may be C.H. CO O PCl It forms crystals [87°] (127° at 11 mm), and 15 sol ether, benzene, and CHCl, but decomposed by water into sali-

cylic and phosphorous acids (Anschutz a Emery, A 239, 301) It is converted by PCI, or free chloring into C,H,Ol,PO, (167° at 11 mm), S G 1557, whence water forms C,H,(OH),PO, [142°] The chloride C,H,ClPO, takes up bromagnetic forms C,H, C,HO, takes up bromagnetic forms C,H, C,HO, takes up bromagnetic forms C,H, C,HO, takes up bromagnetic forms C,H,ClPO, takes up bromagnetic forms contained to the c ine forming C,H,ClBr,PO, (c 187° at 12 mm). 8 Aniline at 210° produces aniline, phenol, and $C_0H_4(OH)$ CONPhH (Limpricht, B 22, 2906) -9 Cyanamide and alcohol at 100° form urea and o oxy-benzoic ether -10 Benzamidine forms a compound C21H18N3O (Pinner, B 23, 3824)—11 Glyceren and gaseous HCl forms C₅H₄(OH) CO OC₅H₅Cl₂ [44°], S G 1 331 (Gottig, B 24, 508), whence sodic salicylate at 180°–200° forms crystalline C₅H₅(O CO C₅H₅OH), and CH(OB₂)(CH₂ O COC₅H₅OH)₂ [95°] (Fritsch, B 24, 779) -12 Acetochlorhydrose forms C ,H30O15 [185°], whence C₂₂H₂₁(OAc),O₅ [111°] (Michael, B 15, 1922) —13 Phenol and SnCl₄ at 120° yield op di oxy benzophenone [144°] (Michael, Am 5,83) -14 Resorcin at 200° forms tri oxy-Orcin gives '(β) oxy-C₆H₄<CO>C₆H₂Me(OH) benzophenone - 15 methyl xanthone' [285°] (Von Kostanecki a Nessler, B 24, 1895) Phloroglucin forms 150 euxanthone $C_6H_4 < CO > C_6H_2(OH)_2 [247^\circ] -17$ When taken internally it is excreted as salicyluric acid or salicyl glycocoll C₀H₀NO₄ [c 160°] (Bertagnini, Il Nuovo Cimento, 1 363)—18 With camphor it forms a compound $C_7H_6O_32C_{10}H_{16}O$ [60°] [a]_D 11 to this a compound of $\Omega_{\rm s}^{\rm log}$ ($\Omega_{\rm s}^{\rm log}$) (Léger, C R 111, 110) —19 $\rm K_2S_2O_7$ (17 pts) added to a solution of salicylic acid (10 pts) and KOH (8 pts) in water (25 pts) forms the crystalline compound $C_2H_4(CO_2K)$ OSO₂K (Baumann, B 11, 1914) — 20 A solution of salicylic acid and borax in water deposits crystals of C₁₄H₁₀NaBO,, whence the corresponding salts NH₄A', KA', MgA', 10aq and CaA' 10aq (Jahns, Ar Ph [3] 12, 212) -21 Chloral at 140° forms C₆H₄<0 OCH CCl₃ [124°] (Wallach, A 193, 1)

Salts —C₆H₄(ONa) CO₂Na With POCl, it gives di phenylene ketone oxide C₁₈H₈O₂ [174°] The normal salt CoH4(OH) CO2Na is converted by POCI, into an isomerio body [91°] (R. Richer, J. pr. [2] 23, 349, 28, 303)—NaHA'₂ Large crystals, sol alcohol (E. Hoffmann, Ar. Ph. [3] 12, 226) —KA' aq Decomposed at 210° into CO₂, phenol, and disodium p oxy benzoate (Ost, pr [2] 11, 392) In presence of excess of KOH the change does not take place The Na salt does not give p oxy benzoic acid when heated alone or with NaOH, but when heated in a current of CO2 at 300° it yields oxy-isophthalic and oxytrimesic acids—NH₄A'—NH₄A'₃aq monoclinic crystals—BaA'₂aq Small needles, sl sol cold water—BaC,H₄O₃2aq Needles, sl sol hot water—SrA'₂2aq—CaA'₂2aq Octahedra, v sol water, sol. alcohol -CaC,H,O, aq. Crystalline powder, nearly insol MgA', 4aq — ZnA', 3aq S 5 at 20° water mga', 4aq — ZnA', 3aq 8 5 at 20° Needles, sol alcohol (Vulpius, Ar Ph [3] 14, 239) — ZnA', 2aq (Marignac, J 1855, 485) — CdA', 2aq — $HgC_1H_1O_2$ (Lajoux a Grandval, J Ph [5] 20, 5]. — HgA', — PbA', 2aq — $PbC_1H_1O_2$, — Oxysalt., $Pb_2O_2(C_1H_1O_2)$, — TlA' — $Tl_2C_1H_1O_2$, — TlOA'. Insoluble powder got by adding sodium salicylate to a solution of bismuth nitrate in glycerin

(Wolff, Ph [3] 14, 508) —AlA', (Van der Velden, becoming violet —MnA'₂2aq —CuA'₂4aq blushgreen needles, v sol water and alcohol.—CuC,H₂O₂aq —Insoluble —CuK₂(C,H₂O₂)₂4aq green tables, v sol water -CuBa(C,H,O,), 4aq (Pellizzari, G 14, 365) -AgA' needles

Methyl ether C₈H₄(OH) CO₂Me Mol w 152 (224° cor) SG ⁹ 1 197 SV 155 9 (Ramsay). 156 7 (Lossen, A 254, 64) HF 129,224 (Stohmann, J pr [2] 36, 353) tutes oil of wintergreen, oil of Gaultheria punc tata and leucocarpa, and oil of birch (Kohler, B 12, 246, Pettigrew, Ph [3] 14, 167) PCl, yields C_sH₄(COCl) O POCl₂ (v supra) Phenyl cyanate at 160° forms C_sH₄(CO₂Me) O CONHPh [238°] (Snape, C J 47, 775) Hydroxylamine hydrochloride yields C.H.(OH) CO NH(OH) [169°] (Jeaurenaud, B 22, 1273) Benzamide forms, on heating, phenyl benzoate and a compound $C_{22}H_{28}N_4O$ [256° cor] crystallising from chloro form in yellow needles (Guareschi, A 171, 143) Forms the crystalline salts C₆H₄(OK) CO₂Me ½aq and BaA'2aq

Oil (Gottig, B 9, 1473) Wr hydrochlorida 14 HF 139.252 With benzamidine hydrochloride it gives (C,H₆O₃)C,H,NO [120°], benzamidine salicylate C₁H₁₄N₂O₃ [202°], and a compound C₂;H₁₅N₃O [246°], whence C₂;H₁₄AcN₃O [141°] (Pinner, B 23, 2935)

Propyl ether PrA' (239°) S G 21 1 021 H F 147,880

Isoamyl ether C₃H₁₁A' (270°) Phenyl ether PhA' Salol [42°] Formed by slowly adding POCl, (28 g) to a mixture of salcylic acid (60 g) with phenol (48 g) at 135° (Seiffert, J pr [2] 31, 472) Anti rheumatic The yield is good (99 g) Timetric tablets (from alcohol, a b c = 963 1 697 (Léger), insol water Its alcoholic solution is coloured violet by FeCl, Conc NaOH forms solid C₂H₄(ONa) CO₂Ph, but boiling NaOHAg saponifies it When heated for boiling NaOHAq saponifies it a long time to boiling it gives CO, phenol, and diphenylene ketone oxide Dissolved in HOAc at is nitrated by HNO, to C₆H₃(NO₂)(OH) CO₂Ph [150°] and a di nitro-compound [183°] HNO, (S G 153) forms also C₆H(NO_{.)}(OH) CO₂Ph [100°] (Knebel, J pr [2] 42, 158)

Nitro-phenoxy ethyl ether C₆H₄(NO₂)O C₂H₄A' The o isomeride [106°] yields an acetyl derivative [80°] The p isomeride crystallises from alcohol in needles [131°] (Wag

ner, J pr [2] 27, 215) Tolyl ethers C.H.MeA' The o, m, and p compounds [35°], [74°], and [39°] are insolwater, sl sol alcohol (Nencki, C R 108, 254)

C₆H₄(OMe) CO₂H Methyl derivative $\stackrel{{
m S}}{{
m G}} \stackrel{{
m 20}}{{
m 1}} \stackrel{{
m 1}}{{
m 1801}} \stackrel{{
m \mu_s}}{{
m 1}} \stackrel{{
m 5521}}{{
m 5521}} \stackrel{{
m R}}{{
m E}_{\infty}} \stackrel{{
m 64}}{{
m 59}}$ [98 5°] S 5 at 20° (Brühl) its methyl ether, which is formed from oil of Wintergreen, KOMe, and MeI (Cahours, A 92, 315) Monoclinic tables (from water) Its aqueous solution is not coloured by FeCl. Yields the salts BaA', PbA', aq, and AgA', and the ethers MeA' (228°), EtA' (235°) (Fölsing, B 17, 486), and PhA' [59°] (Seiffert, J pr [2] 31,

Cu₂A'₄(OH), and AgA' (Kraut, A 150 1) and the ethers MeA' (245°) and EtA' (251°)

Isopropyl derivative C.H.(OPr) CO H Oil, forming the salts Cah', 2aq, Bah', aq, and Agh' aq and the ether Mah' (250°)

Allyl derivative C₆H, (OC, H₃) CO₂H

[113°] Forms the sait Aga and MeA' (245°) (Scichilone, G 12, 449). Forms the salt AgA' and the ether

Ethylene derivative C2H4(O'C2H4 CO2H)2. [152°] Formed by saponification of its ethyl ether Et₂A" [97°], which is itself got by heating C.H.(ONa) CO.Et with ethylene bromide at 130° Silky needles (from water) (Weddige, J pr [2] 21, 128)

derivative C₆H₁(OPh) CO₂H Phenyl Formed by adding Na to (355°) [113°] $C_{\rm g}H_{4}(OH)CO_{2}Ph$ at 300° (Graebe, B 21, 502), and also by the action of phenol on o-diazo benzoic acid (Griess, B 21, 982) Plates, v sl sol hot water Heated with cone H₂SO₄ it yields diphenylene ketone oxide Heating with baryta forms diphenyl oxide [25°] Bromine water at 150° forms C₆H₂Br₂O C₆H₄CO₂H [176°], whence AgA' and EtA' [57°] (Arbenz, A 257, 86) HNO, at 0° forms a d nitro-derivative [153°], which gives the salts BaA'₂4aq, CaA'₂4aq, and AgA', and the ethers MeA' [126°], EtA' [76°], and an amide [166°] The phenyl derivative [166°], and an amide [166°] The phenyl derivative [166°]. tive of salicylic acid forms the salts NH,A', KA', CaA'₂2aq, BaA'₂aq, and AgA', and the ether, MeA' and EtA', boiling above 360°, and PhA' [109°]

Nitro-phenyl ethylene derivative C₆H₄(NO₂) OC₂H₄O C₆H₄ CO₂H. The o- acid [142°-148°] forms a crystalline ether Et A' [c 100°], and the p acid [132°] forms a similar ether EtA' [81°] (Wagner, J pr [2] 27, 214) The o- acid yields on reduction an amido acid [110°], forming C₁₅H₁₅NO, HCl [177°]

Benzyl derivative C, H, CH2O C, H, CO, H.

°] Tables (Perkin, A 148, 27) —AgA'
Tolyl derivative Occurs in natural sali cylic acid (J Williams, Ph [3] 8, 785)

Acetyl derivative C₆H₄(OAc) CO H [118°] Formed from the acid and AcCl (Kraut, A 150, 9) Needles (from water), v sl sol cold water Hydrolysed by alkalis, but not by boiling water

Benzoyl derivative C.H.(OBz) CO.H The crystalline methyl ether MeA' is formed from methyl salicylate and BzCl (Gerhardt, A Ch [3] 45, 104)

Amide C.H. (OH) CONH. [139°] From the ethers and NH,Aq (Limpricht, A 98, 258) Formed by the action of AcCl on o-oxy benzald oxim (Classen a Stock, B 24, 138) Plates and tables Gives saligenin on reduction with sodium amalgam (Hutchinson, C J 57, 957) With bromine water it yields C₆H₂Br₂(OH) CONH₂ [183°] (Spilker, B 22, 2769) When heated in a current of HCl it forms (C.H.(OH) CO), NH [199°], which yields (C,H,O,),N. (C,H,10O,),HCl—AgA' flocculent pp (C,H,O₂),NAg

Bensoyl derivative of the amide C₆H₄(OBz) CONH₂. [200°] Needles, sl sol.

alcohol

Cumenyl derivative of amide [200°] 17, 486), and PhA' [59°] (Senfert, J pr [2] 81, Methyl derivative of the amide C.H. (OMe) CONH. [129°] Prisms (from ether) (Grimaux, Bl. [2] 13, 26) The homolity 4°] Forms the salts CaA', BaA', PbA', 2aq, logous ethyl derivative [110°] (Limpricht, A. 98. 264) and isopropyl derivative are crystalline

[1849] Anilide C,H,(OH) CONHPh Prisms (from dilute alcohol) (Wanstrat, B 6, 336, Kupferberg, J pr [2] 16, 442, Hübner a Meusching, A. 210, 341) FeCl, colours its alcoholic solution violet. On heating with sulphur

at forms C₆H₄<^N>C C₆H₄OH [129°] (Hofmann,

B 13, 1237) Yields on nitration

C.H.(NO2)(OH) CONHPh [224°] Forms the salts

KC12H10NO2 23aq and TlO12H10NO

Nitro-anilide C.H.(OH) CO NHC.H.NO. The c., m., and p-varieties melt at 154°, 218°, and 280° respectively

p-Tolurde C.H.O. NHC.H., [156] Prperidide C.H.(OH) CO NC.H. [1569] Yellowish tables (Schotten, B 21, 2252)

Hydroxylamids C.H. (OH) CO NH(OH). [169°] Needles Yields Pb(C,H. NO.) 24aq (Jean-

renaud, B 22, 1270)

Anhydride O(C₆H₄CO₂H)₂ Disalicylic acid Formed, together with salicylide, by the action of POCl, on dry sodium salicylate (Gerhardt, A. Ch [3] 37, 322) Amorphous mass, v sol alcohol and ether Gives no colour with FeCl. Dissolves unchanged in aqueous Na₂CO₂ Boiling KOHAq converts it into salicylic acid An anhydride C₅H₂O₁, is formed by heating sodium salicylate (3 pts) with POCl₂ (1 pt) at 150° (Kraut, A 150, 13) It is insol cold alcohol A third anhydride C₂₈H₁₈O₉ is got by heating C₆H₄(OAc) CO₂H at 200°-240° (Kraut) It is sol alcohol, and softens at 70°

Internal anhydride C,H,O, or C,H,O, e. $C_eH_4 < {0 \atop CO} {CO \atop O} > C_eH_4$ Salicylide [195°-200°] Formed as above Nodular groups of plates from alcohol) (Schiff, A 163, 220) Insol water, al sol alcohol Not attacked by AcCl Reconverted by potash into salicylic acid A resinous anhydride C₂₈H₁₈O₂, accompanying salicylide is still less soluble in alcohol

Nutrule C.H. (OH) CN. o-Cyano-phenol [98°] Formed by the action of P.O. or P.S. on the amide, and also from C₆H₄(OH) CH NOH and Ac₂O (Miller, B 22, 2771, 2797, Tiemann, B 20, 3082, Meyer, B 20, 3289, cf Grimaux, Bl [2] 13, 26, Ahrens, B 20, 2953) Formed also from diszophenol chloride by Sandmeyer's In most of these preparations it is accompanied by a small quantity of a substance melting at 195° Needles, v sol alcohol, m sol Coloured violet by FeCl. **c**old water Gives a white crystalline pp. with bromine water Gives a methyl derivative C.H. (OMe) CN (256°), and an ethyl derivative C.H. (OEt) CN [258°) which may be got from C.H.(OEt)NH. (Pinner, B 23, 2952) The acetyl derivative C.H.(OAc) CN is an oil (258°) (Lach, B 17, 1572) while the bensoy l derivative C.H. (OBz) CN [149°] is crystallus (Limpricht, A 99, 250, Henry, B. 2, 491)

Polynstrile (C.H. (OH) CN) [296°-299°] Obtained by heating the amide to 270° (L) and as a by-product in preparing the nitrile (Miller, B 22, 2798) Yellow needles, insol alcohol, al sol ether. Decomposed by HCl at 200° into

CO₂, phenol, and NH

m-Oxy-bensoic acid C,H,(OH) CO,H [200°]. S. 87 at 0° (Ost), 9 at 18° (Fittica, B 11, 1208).

HF 111,000 (Von Rechenberg); 136,000 (Stohmann, J pr [2] 40, 129) Pi C 729,000

Formation -1 By the action of nitrous acid on amido benzoic acid (Gerland, A 91, 185, Graebe a. Schultzen, A 142, 850) —2 By fusing sulpho-benzoic acid with potash (Barth, A 148, 80) -8 By potash fusion from m chloro benzoic acid (Dembey, A 148, 222), m cresol, and even benzoic acid (Barth, A 154, 361, M 3, 802)

Properties - Nodular groups of needles (from water) May be distilled V sol boiling water and alcohol Volatile with steam Blackens when quickly heated to 300°, but gives no phenol When the soid (2 mols) is heated with baryts (3 mols) at 350° it forms no phenol un less the baryta is used in large excess (7 mols) (Klepl, J pr [2] 27, 159) It tastes sweet solutions are not coloured by FeCl, Iodine and KOHAq, followed by an acid, give a coffee-brown pp (Messinger, B 22, 2321) It is not acted upon by hydroxylamine

Reactions -1 Bromine (3 mols) forms tribromo-m-oxy benzoic acid, soluble in water (Werner, Bl [2] 46, 276) -2 Sodium amalgam reduces it, in acid solution, to m oxy benzy alcohol —3 Conc H2SO, forms, on heating, several dioxy anthraquinones $(q \ v)$ benzoic acid is also present, the two oxy an thraquinones are also formed —4 Heated with cinnamic acid and H₂SO₄ it yields anthracou marin C16HaO3 [260°] (v CINNAMIC ACID, Reaction 14) -5 By nitration with dilute nitric acid, which takes place extremely readily, it yields mixture of three nitro oxy-benzoic acids $C_0H_3(NO_2)(OH)CO_2H[4\ 3\ 1],\ [2\ 3\ 1],\ and\ [5\ 3\ 1]$ (Gress, $B\ 20,\ 403)$ —6 PCl₃ forms the chloride C_sH₄(COCl) OPOCl₂ of m-carboxy phenyl phos phoric acid (q v) -7 The K salt heated with K₂S₂O₇ forms SO₃K₂O C₆H₄CO₂K [220°-225°] (Baumann, B 11, 1915)—8 When taken internally, it appears in the urine as oxybenzuric acid CoH4(OH) CO NH CH2 CO2H, crystallising in needles (Baumann a Herter, H 1, 260)

Salts.—NH,A' needles, v sol cold water -CaA'₂3aq m sol water -BaA'₂ gummy -TlA' -Tl₂C₇H₄O₂ -PbA'₂ -CdA'₂ -CuA'₂ aq green needles

derivative C₆H₄(OAc) CO₂H Acetyl [127°]

Ethyl ether EtA' [72°] (282°) Tables from water), nearly insol cold water Conc (from water), nearly misor
NaOHAq forms crystalline C₈H₄(ONa) CO₂Et

Mathul derivative C₈H₄(OMe) CO₂H

[107°] Formed from its methyl ether, and also by oxidising CH, C,H, (OMe) with KMnO, (Oppen heim a Pfaff, B 8, 887) Formed also by the action of CO, and Na on C,H, Br(OMe) (Körner, Bull Acad Belg [2] 24, 155) and by boiling the sulphate of m-diazobenzoic acid with MeOH (Griess, B 21, 979) White needles, v sl sol cold water It forms the salts CaA', aq and AgA' and the ether CaH4(OMe)CO2Me which is formed by heating m-oxybenzoic acid with KOH and MeI at 140°

EthylC.H.(OEt).CO2H. derivative Formed from its ethyl ether **୮187**℃ C.H. (OEt) CO.Et (263°) (Heintz, A 153, 331) or by boiling the sulphate of diazo-benzoic acid with alcohol (Fittics, B 11, 1209, Griess, B 21, Yields CaA', 2aq, BaA', 2aq, 979) Needles.

and AgA'.

Allyl derivative C₂H₄(OC₂H₅) CO₂H [148°] Colourless lamins Its ethyl ether is a thick pungent oil (284°) (Scichilone, G 12, 449)

Ph. nyl derivative C_aH₁(OPh) CO₂H [145^o] Formed by the action of phenol on the sulphate of m-diazo benzoic acid (Griess, B 21, 980) Needles, almost insol hot water Yields BaA', 3[§]aq

Yields Bah', 3\(\frac{3}{2}\) and

Amide C₀H₄(OH) CONH₂ [167°] Formed from the ether and conc NH₂Aq (Schulerud, J pr [2] 22, 290) Thin plates (from water), sol alcohol and ether, insol chloroform

Anrilde C₆H₁(OH) CONHPh [155°] Needles, insol water (Kupferberg, J pr [2] 16,

Nitrile C_cH₄(OH) CN [82°] Formed by the diazo- reaction from C_cH₄(NH_c) CN by displacing NH_c by OH (Griess, B 8, 859) or from C_cH₄(NH_c) OH by displacing amidogen by Cy (Ahrens, B 20, 2953) Plates (from water) with intensely sweet taste Its acetyl derivative C_cH₄(OAc) CN [60°] is got by boiling moxybenzaldoxim with Ac_cO (Clemm, B 24, 827)

Anhydride $C_{14}\ddot{H}_{10}O_{5}$ Formed, together with an anhydride $C_{26}H_{24}O_{17}$ [165°] by the action of POCl₃ at 45° on *m*-oxy benzoic acid (Schiff, B 15, 2588) Minute crystals, sol boiling alco

 $Tetra-hydride CH_2 < \stackrel{CO}{CH_1CH_2} > CH CO_2H$

Formed by warming the tetrahydride of oxyterephthalic acid with water (Baeyer a Lutein, B 22, 2183) Mixes with water Forms the hygroscopic salt NaA' crystallising in slender needles Yields an oxim C,H₁₁NO₂ [170°] and a phenyl hydrazide C₁,H₁₈N₂O₂ [125°]

p Oxy benzoic acid C₈H₄(OH) CO₂H [213°] S 173 at 0° (Ost, J pr [2] 17, 230), S at 15° (Saytzeff) H F 113,000 (Von Rechenberg), 139,100 (Stohmann, J pr [2] 40, 130) H C

725,900

Formation -1 By heating anisic acid with cone HIAq at 130° for 12 hours (Saytzeff, A 127, 129) —2 By the action of nitrous acid on p amido benzoic acid (G Fischer, A 127, 145) 3 By potash fusion from p sulpho benzoic acid (Remsen, Z [2] 7, 81, \hat{A} 178, 281), anethol (Ladenburg, A Suppl 8, 87), anisic acid (Barth, Sitz W 54 [2] 633), gum benzoin, acaroid resin (Hlasswetz a Barth, A 134, 265, 138, 61), tyrosine (Barth, A 136, 110, Ost, J. pr [2] 12, 159), carthamin (Malin, A 136, 115), phloretic acid, p cresol, and even benzoic acid (Barth, A152, 96, 154, 559, 164, 141, M 3, 802)—8 By passing CO₂ through C₄H₂OK dissolved in boiling phenol, or, better, by heating C₄H₂OK in a current of CO₋₂ at 170°-210° (Kolbe, J pr [2] 8, 36, 10, 89, 451, 11, 24, 0st, J pr [2] 11, 385, Hartmann, J pr [2] 16, 35) At 130°-150° the product is salicylic acid—4 The basic salt C.H.(OK) CO.K is formed, together with CO. and phenol, by heating potassium (but not sodium) salicylate at 220° A mixture of salicylic acid (1 mol) and excess of KOH (8 mols.) is not affected at 250°, but at 800° yields only K,CO, and C.H.OK -5 Together with a smaller quantity of salicylic acid by heating phenol with alcoholic potash (or soda) and CCl. The reaction takes place less quickly in aqueous solution (Tiemann a Reimer, B 9, 1285; Hasse, B10, 2186)

Properties — Monoclinic crystals (containing aq), a b c=1 370 1 1 102, $B=105^{\circ}$ 26° V sol. hot water, alcohol, and ether, sl sol chloroform (unlike salicylic acid) and CS₂ (unlike benzoic acid) Split up at 220° into CO₂ and phenol With iodine and potash it gives a pale-red pp, which becomes yellow on acidifying (Messinger a Vortmann, B 22, 2321) Not attacked by hydroxylamine With FeCl₃ it gives a yellow amorphous pp Excess of bromine water gives CO₂ and tri-bromo phenol

Reactions —1 p-Oxy benzoic acid (1 mol.) is converted by PCl, (1 mol.) into C,H,Cl,PO, re C,H,(COCl)OPOCl, (176° at 14 mm) SG 20 This chloride shows the following reac tions (a) Water forms p carboxy-phenyl phos phoric acid C₆H₄(CO₂H)OPO(OH)₂ which forms plates [200°], v sol water, alcohol, and ether It is not decomposed by boiling aqueous KOH, but water at 160° forms phosphoric acid and poxy benzoic acid (b) Distillation under atmo spheric pressure somewhat decomposes it (c) The chloride (1 mol.) heated with PCl, (1 mol.) at 160° forms p chloro benzoyl chloride, at 160° forms p chloro benzoyl chloride, C_eH_{*}Cl COCl (Anschutz a Moore, A 239, 342) 2 On distillation half of it splits up into phenol and CO₂, the rest yields several anhydrides —3 The K salt when distilled yields diphenylene oxide, di-phenylene-ketone oxide, and phenol (Goldschmiedt, M 4, 127) -4 Yields 50 or 60 pc of the theoretical amount of phenol on fusion with NaOH (Barth a Schreder, B 12, 1257) -5 The Na salt heated in a current of ${
m CO}_2$ at 290° yields salicylic acid (Kupferberg, J pr [2] 16, 424) -6 The Ca salt on dry distillation yields phenol, CO2, salicylic acid, oxyisophthalic acid, diphenylene oxide, and diphenylene ketone oxide -7 H.SO, at 100° forms C₀H₃(OH)(SO₃H) CO₂H (Klepl, *J* pr [2] 28, 196) —8 The K salt heated with K₂S₂O, forms C₈H₄(CO.K) O SO₃K (Baumann, B 11, 1916) -9 Taken internally it appears in the urine as p oxy benzuric acid C₂H₂NO₄ [c 228°]

Salts — NaA', 5aq very soluble efflorescent plates — NaA', 5aq very soluble efflorescent plates — Na,C,H,\(\hat{O}\), — KA' 3aq — NH,\(\hat{A}\)' aq long efflorescent prisms — CaA', 4aq slender needles — BaA', 2aq flat needles — BaA', 2aq rhombohedra — BaC.H,\(\hat{O}\), sandy powder — TlA' — CdA', 4aq — CdA', 6aq — ZnA', 2aq — PbA', 2aq — ChA', 4aq — CdA', 6aq — ZnA', 2aq

CuA', 6aq —AgA' 2aq
Acetyl derivative C.H. (OAc) CO.H.
[185°] By heating the acid with Ac. O Silvery

plates (from CHCl₃)

Methyl ether MeA' [117°] (283°). HF 138,800 Formed from the acid, KOH, and MeI (Ladenburg a Fitz, A 141, 250) Large tables (from ether), v sl sol hot water

Ethyl ether Eth' [112 5°] (G), [116°] (Hartmann) (298°) HF 147,690 Formed from the acıd, alcohol, and HCl (Graebe, A 139, 134). Crystalline Yields solid C,H,(ONs) CO,Et

Crystalline Yields solid C₈H_{*}(ONa) CO₂Et Phenyl sther PhA' [176] Present in the volatile product of the destructive distillation of p oxy-benzoic soid (Klepl, J pr [2] 26, 214) Trimetric tablets (from chloroform) Saponified by cold NaOHAq With alcohol and HCl it yields phenol and p oxy benzoic soid The acetyl derivative C₂H_{*}(OAc) CO₂Ph orystallises in long plates [84°]

Methyl derivative C.H. (OMe) CO.H. Anisic acid Mol w 152 [184°]. (275°-280°).

04 at 18° HCp 895,200 H.F 132,800 (Stohmann, J pr [2] 40, 181) Formed by oxi dation of anise-camphor, and of oils of anise, fennel, and tarragon, being derived from the anethol contained therein (Cahours, A Ch [3] 2, 287, 14, 483, 28, 351, 25, 21, 27, 489, Laurent, Rev scient 10, 6, 362, Gerhardt, A Ch [8] 7, 292, Ladenburg, A 141, 241) Obtained also from its methyl ether, which is formed by heating p oxy benzoic acid (1 mol) with KOH (2 mols) and MeI (2 mols) at 120° (Ladenburg) It is a product of the oxidation of chica (Erd mann, J pr 71, 198) It is also produced by It is also produced by oxidising C.H.Me(OMe) (Körner, Bl [2] 10, 468) and by boiling the sulphate of p diazobenzoic acid with MeOH (Griess, B 21, 979) Prepared by mixing basic potassic p oxybenzoate (got by heating potassic salicylate at 220°, or by adding KOH to a solution of p oxybenzoic acid) with a solution of KMeSO, and evaporating to dryness The residue is treated with HCl, and the anisic acid separated from undecomposed p oxybenzoic acid by solution in chloroform (E v Meyer a P Richter, J pr [2] 32, 429) Monoclinic prisms, m sol hot water Yields, on nitration, $C_6H_3(NO_2)(OMe)CO_2H$, $C_6H_3(NO_2)_2OMe$, C₆H₂(NO₂)₃OMe HIAq converts it into MeI and p-oxy-benzoic acid (Graebe, A 139, 148) When taken internally it passes into the urine as anistaken internally it passes into the unne as ansurine acid (q v). POCl₂ forms the anhydride $C_1H_1O_2$ [99°] (Pisani, A 102, 284) PCl₃ forms crystalline C_2H_4 (OMe) COCl Forms the salts NH₄A', KA', NaA' $\frac{1}{2}$ aq, NaA' $\frac{5}{2}$ aq, BaA' $\frac{2}{2}$ s, SA' $\frac{2}{2}$ aq, CaA' $\frac{2}{2}$ aq, Pb(OH)A', Cr $\frac{2}{2}$ A' $\frac{3}{2}$ aq, CoA' $\frac{2}{2}$ 3aq, NiA' $\frac{2}{2}$ 3aq, CuA' $\frac{3}{2}$ 3aq, CuA' $\frac{2}{2}$ 3aq, CuA'MeA' [47°], (255°) and EtA' (c 255°) Its amide C₈H, (OMe) CONH₂ [163°] is formed by the action of NH, on C,H, (OMe) COCl It is also formed by passing cyanic acid vapour and dry HCl through C.H.OMe containing AlCl,, and by the action of ClCONH, and AlCl, on C.H. OMe dissolved in CS₂ (Gattermann, A 244, 62, B 23, 1197) It crystallises from water in needles or plates. The anilide C₆H₄(OMe) CONPhH [169°] is formed by the action of phenyl cyanate on anisole containing AlCl, (Leuchart a Schmidt, B 18, 2338) The nitrile C.H. (OMe) CN, [62°], (254°), is formed by heating the amide alone or with PCl_s (Henry, Z [2] 6, 209, B 2, 667), and by heating C.H. (OMe) CH NOH with Accl at 115° (Miller, B 22, 2791) It crystallises in needles, v sol alcohol and ether Hydroxylamine converts it into C₆H₄(OMe)C(NH₂)NOH [123°]

Ethyl derivative C₆H₄(OEt) CO₂H [195°] Formed from its ether EtA' (275°) which is got from p-oxy benzoic acid, KOH, and Eti (L a F) Got also by oxidising the ethyl derivative of phloretic acid with chromic acid mixture (Körner a Corbetta, B 7, 1731), and by boiling the sulphate of p diazo-benzoic acid with alcohol (Griess, B 21, 980) Needles Yields AgA' crystallising in needles The amide C₂H₄(OEt) CONH₂ [202°] (G), [206°] (P), is formed by the action of cyanic acid or ClCONH₂ on C₂H₄OEt in presence of AlCl₂ (Gattermann, 4.244, 63, B 23, 1197), and by adding NaOHAq to p-ethoxy-benzamidine hydrochloride (Pinner, B 28, 2954) The anilide C₂H₄(OEt) CONHPh [170°] is formed by the action of phenyl cyanate

on phenetole in presence of AlCl₃ (L a S) The nitrile C_bH₄(OEt) CN [69°] (258°), is got from C_bH₄(OEt) NH₂ by Sandmeyer's reaction (Pinner, B 23, 2953) It is volatile with steam

Ethylene derivative The amide C₂H₄(OC₂H₄ CONH₂)₂ [280°] is formed by the action of ClCONH₂ on C₂H₄(OPh)₂ in CS₂, in presence of AlCl₃ (Gattermann, A 244, 69)

Allyl derivative C₄H₃O C₆H₄CO H [123°] Formed from its ether EtA' [109°] (260°) which is got by heating p oxy-benzoic ether with KOH and allyl iodide at 120° (Soichilone, G 12, 451)

Phenyl derivative C₅H₄(OPh) CO₂H [160°] Obtained by the action of phenol on the sulphate of p diazo benzoic acid (Griess, B 21, 980), and also by the action of boiling alcoholic potash upon C₅H₄(OPh) CO₂Ph, a white sublimate [73°-78°] got by strongly heating p oxybenzide in a current of hot CO₂ (Klepl, J pr [2] 28, 200)

Phenoxy-ethyl derivative C₂H₄(OPh) O C₂H₄ CO₂H [196°] Satiny needles (from alcohol) (Wagner, J pr [2] 27, 227) Its ether EtA' [81°] is crystalline

Nitro-phenoxy-ethyl derivative C₅H₄(NO₂) O C₅H₄O C₆H₄CO₂H The o-compound [207°] forms an ether EtA' [103°] crystal lising from alcohol in plates, and may be reduced to C₆H₄(NH₂) O C₂H₄O C₆H₄CO₂H [185°] The p-isomeride [218°] forms a salt NaA'3aq and an ether EtA' [181°] crystallising in minute needles

Amide C₆H₄(OH) CONH₂ [162°] Needles (containing aq) Forms the sodium compounds C₆H₄(ONa) CONH₂ and C₆H₄(ONa) CONH₄Cl [206°] Yields p oxy benzyl alcohol on reduction with sodium amalgam (Hutchinson, B 24, 175)

Anilide C₈H₄(OH) CONPhH [197°] Yellow plates, v sol alcohol

Priperidide C₆H₄(OH) CONC₅H₁₀ [210°] Prisms (from dilute alcohol) (Schotten, B 21,

2254) Nitrile $C_eH_4(OH)$ CN p-Cyanophenol [113°] Formed by distilling ammonium p oxy benzoate with P_2O_s (Hartmann) Formed also from p amido phenol by Sandmeyer's reaction (Ahrens, B 20, 2954), and by the action of NH₃ on p-oxy benzide Thin trimetric lamine, a b c = 855 1 2 308 M sol hot water Forms an acetyl derivative $C_eH_4(OAc)$ CN, [57°], (266°), crystallising in white needles

Anhydrade C,H_1O_2 p-Oxybenzide Left in the retort after distilling p-oxy benzoic acid below 850° (Klepl, J pr [2] 25, 525, 28, 194) White amorphous powder, blackening at 350° without melting Insol alcohol Reconverted into p oxy-benzoic acid by boiling KOHAq, not attacked by NH₂ or Na₂CO₂Aq Heated in sealed tubes with PCl₂ it yields C_2H_1 C? CCl₂

attacked by NH₂ or Na₂CC₂Aq Heated in sealed tubes with PCl₂ it yields C₆H₄C! CCl₂

Anhydrids C₁H₁₀O₃ is

CO₂H₂C₄H₄ O CO C₆H₄ OH [261°] A product of the action of heat on p oxy benzoic acid Minute needles, v sol alcohol Quickly converted by alkalis into p-oxy-benzoic acid Yields

verted by alkalis into p-oxy-benzoic acid Yields
NaA', BaA', and C₁,H₂AcO₂ [217°]

Anhydrids C₂,H₂,O, i.e.
CO₂H₂,O CO₂H₂,O H₃ [280°] S
(alcohol) 45 in the cold, 13 at 78° Accompanies p oxybenzide. Crystalline powder Con

verted by potash into p oxy benzoic acid Gives

NaA' and C₁₁H₁₂Ac₁, [230°]

Anhydride (H₁₁O, Formed from the cold and POCl₂ (Schiff, B 15, 2588) Insoluble powdern

D1-oxy benzoic acid C,H,O, 1e

J.A. (OH) CO.H [3 2 1] Pyrocatechin carboxylic Mol w 154 [204°] Formed in small quantity, together with protocatechnic acid by neating pyrocatechni (1 pt) with ammonium carbonate (4 pts) and water (5 pts) at 140° (A Miller, C J 41, 398, A 220, 116) Formed Formed also by heating iodosalicylic acid with KOH Needles (containing 2aq), m sol water, v sol alcohol and ether FeCl₂ gives a blue colour not destroyed by excess, but changed to violet red by Na₂CO₃ Gives a flocculent pp with Pb(OAc)₂ — BaA'2 5aq prisms (S of BaA'2) 1 at 18°

Isomeride v PROTOCATECHUIC ACID

s D1 oxy benzoic acid C₆H₄(OH)₂CO₂H[5 3 1]
(a) Resorcylic acid [222°] (B a S), [233°] (B) Formed by fusing s di sulpho benzoic acid with potash (Barth a Senhofer, A 159, 222) Formed also from bromo sulpho benzoic acid by potash-fusion (Böttinger, B 8, 374) Prisms or needles (containing 1; aq), m sol cold water Gives no colour with FeCl₃ Conc H₂SO₄ at 140° forms a red solution whence water ppts green flakes of anthrachrysone C.H.O. Yields resorcin on anthrachrysone C₁₄H₈O₆ fusion with potash

Salts - NaA'aq - BaA', 4aq - CuA', 6 aq -

CdA'₂4'aq —AgA'aq crystalline pp Ethyl ether LtA' [below 100°] Prisms Methyl ether of the methyl deriva tive C₆H₃(OH)(OMe)CO₂Me (315°) Formed, together with CoHq(OMe) CO2Me from s di oxy benzoic acid, MeI, and KOH (Meyer, M 8, 430)

Dr methyl derivative C, H3(OMe).CO.H [176°] Formed by methylation and also by oxidation of the di methyl ether of orcin (Tie mann a Streng, B 14, 2002) White needles, sol hot water —AgA' crystalline pp

Methyl ether of the di methyl deri-C₆H₃(OMe) CO₂Me [81°] (298°)vative

Four sided prisms (M)

Di ethyl derivative C.H. (OEt)2CO2H [88°] Prisms Forms oily C.H. (OEt) CO.Lt

Di oxy benzoic acid C₆H₃(0H)₂CO₂H [4 2 1] (β) Resorcylic acid [205°] S 26 at 17° H F HCp 676,900 (Stohmann, J pr [2] 188,100 40, 132)

Formation -1 From C.H.Me(OH)(SO,H) [1 2 4] by heating with KOH (Ascher, A 161, 11) 2 From toluene disulphonic acid by oxidation and potash fusion (Blomstrand, B 5, 1088, Fahlberg, Am 2, 196) -3 By oxidation of its aldehyde or of umbelliferone (Tiemann a Reimer, B = 12,997, 13,2358) - 4 By heating resorom with ammonium carbonate and water at 125° (Brunner a Senhofer, B 13, 2356) —5 By oxidising morin with HNO, (Benedikt a Hazura, M 5, 170) -6 By warming C₆H₃(OH)₂CS₂H with acid (Lippmann, M 9, 306, 10, 620)

Preparation -20 pts of resorem are heated for an hour and a half with a solution of 100 pts of potassium or sodium hydric carbonate in 200 grms of water, the yield is 80 p c of the resorcin (Bistrzycki a Kostanecki, B 18, 1984)

Properties - Crystallises from ether in needles (containing 8aq) and from water in

prisms (containing laq, 1 laq, or 2 laq) Decomposes at its melting point into CO₂ and resoron FeCl₂ colours its solution dark rose red Bleaching powder gives a violet tint, changing to brown By treating the acid with C₆H₃(OH)₂CO₂H [5 2 1] and Ac₂O and distilling the product there is formed euxanthone $\begin{bmatrix} 4 & \frac{1}{2} \end{bmatrix} C_0 H_3(OH) < \begin{matrix} CO \\ O \end{matrix} > C_0 H_3(OH) \begin{bmatrix} 1 \\ 2 \end{bmatrix} 5 \end{bmatrix}$ (Graebe, B 22, 1405)

Salts - KA'aq - BaA', 4aq - BaA', 7aq -

CuA'28aq -AgA'

o Methyl derivative $C_6H_3(OH)(OMe)CO_2H$ [4 2 1] Formed by oxidising C_cH₃(OAc)(OMe)CHO (Tiemann a Par-risius, B 13, 2354) Crystalline Sol water. Gives no colour with FeCl,

p Methyl derivative

C.H.(OMe)(OH)CO.H [421] [154°] S 7 at 20° Got by partial methylation of the acid (T a P), and also by the action of CO2 on C₆H₄(ONa)(OMe) at 215° (Korner a Bertoni, Rendiconti d R Istit Lombardo, 13, 741, B 14, 847) Needles, sol hot water Gives a reddish-violet colour with FeCl, -NaA'aq -KA' -BaA'24aq -PbA'2aq

Dr-methyl derivative C_aH₃(OMe)₂CO₂H [108°] Got by methylation (T a P) and by oxidation of the dimethyl derivative of (β) methyl umbellic acid (Pechmann, B 16, 2126, 17, 2133) Needles, sl sol cold water - CuA'.

-PbA'. -AgA' white pp

Di ethyl derivative C.H. (OEt) CO2H. [99°] Got from the aldehyde (Tiemann a.

Lewy, B 10, 2215)

Di oxy benzoic acid C₆H₃(OH)₂CO₂H [6 2 1] [c 147°] Formed, together with the (4,2,1)isomeride, by heating resorcin with ammonium carbonate and water (B a S) Obtained also from the methyl derivative of the nitrile (Lobry de Bruyn, R T C 2, 205) Needles Decomposes on fusion into CO2 and resorcin FeCl. gives a violet colour, changed to blue by excess. Bromine water gives tri bromo resorcin—BaA' aq—CuA', 8aq—AgA' crystalline pp
Di-methyl derivative CoH, (OMe), CO, H.

[179°] Tables (from alcohol)

Nitrile of the di-methyl derivative C.H.(OMe),CN [118°] (310°) Formed from C.H. (OMe) (NO.) CN by boiling with MeOH and KOH Crystals Gives with nitric acid a nitro- compound C₀H₈N₂O₄ [111°] The corresponding nitriles C₀H₃(OMe)(OEt)CN [66°] and C₆H₃(OEt)₂CN [122°] crystallise from alcohol, the former in trimetric crystals, abc = 796 1 1 65, and the latter in di metric crystals a c = 1 565 (Lobry de Bruyn, R T C 3, 383)

Di oxy benzoic acid C₆H₃(OH)₂CO₂H [5 2 1]. Gentisic acid Hydroquinone carboxylic acid.

[197°]

Formation -1 By fusing iodo salicylic acid [196°] or brome salicylic acid with KOH (Lautemann, A 120, 299; Bakowsky a Leppert, B 8, 789, Miller, A 220, 124, P F Frankland, C J. 37, 750) —2 From oxy amido-benzouc acud (Goldberg, J pr [2] 19, 371) —3 By fusing gentisin with potash (Hlasiwetz a Habermann, A 175, 66, Tiemann a Miller, B 14, 1988) -4 By digesting KHCO₂ (4 pts) with hydroquin one (1 pt.) and water (4 pts) (Senhofer a Sar lay, M 2, 448)

Properties - Needles or prisms, v sol water, ! alcohol, and ether FeCl, colours its solution blue Reduces Fehling's solution on heating Split up on distillation into CO2 and hydroquinone Benzamidine forms a compound [266°] (Pinner, B 23, 2939)

Salts —NaA', 5\(\frac{1}{2}\)aq Deliquescent prism —KA'aq —CaA', 7aq —BaA', S 40 at 18° -PbA, 2aq —CuA', 4\(\frac{1}{2}\)aq Ethyl ether EtA' [75°] Crystals Deliquescent prisms

m-Methyl derivative C₆H₄(OH)(OMe)CO₂H [2 5 1] [142°] S 17 at 10°, 9 at 100° Formed by oxidising the acetyl-methyl derivative of gentisic aldehyde CaHa(OAc)(OMe)CHO with KMnO4, and saponi fying the product (Tiemann a Miller, B 14, 1997) Formed also by the action of CO₂ at 225° on C₆H₄(ONa)(OMe) (Korner a Bertoni) Needles Its solution is coloured blue by FeCl.

Di-methyl derivative C₆H₁(OMe)₂CO₂H [76°] Formed by oxidising C₆H₂(OMe)₂CHO Needles—AgA' small white needles

Tri-oxy-benzoic acid v Gallic acid

Tri-oxy benzoic acid C₆H₂(OH),CO₂H

Tri-methylderivative C₆H₂(OMe)₃CO₂H [109°] Formed by oxidising the tri methyl derivative of asculetic acid (Will, B 16, 2113)

Tri-ethyl derivative C.H. (OEt), CO2H [134°] Formed by oxidation of the tri ethyl derivative of (a) or (β) esculetic acid with $KMnO_4$ (W) Slender needles

Tri oxy-benzoic acid

C₆H₂(OH), CO₂H [4 3 2 1] Mol w 170 220°] S 13 at 12 5° H F 231,300 [206°-633,700 (Stohmann) Formed, together with pyrogallol dicarboxylic acid, by heating pyrogallol with ammonium carbonate (Senhofer a Brunner, M 1, 474, Kostanecki, B 18, 3202, Schiff, A 245, 35) Needles (containing §aq), sol alcohol FeCl, colours its dilute solution violet Bleaching powder and nitric acid do the Lime and baryta water gives a bluish Reduces ammoniacal AgNOs in the cold H₂SO₄ does not form rufigallic acid (difference POCl_s forms an acid C₁₄H₁₀O₉ from gallic acid) greatly resembling tannin It is an astringent yellow powder and gives Ba(C14H2O2)2 and C, H,Ac,O,

Salts —KA'aq —NaA' 2aq —BaA', 5aq —
CaA', 4aq —Pb_C, H_2O, 1\frac{1}{2}aq white flocculent pp
Methyl ether C, H_2(OH), CO_Me [152]

Needles (containing 2 aq)

Tri-methyl derivative C₆H₂(OMe),CO₂H

[99°] Crystals (Will, B 21, 2020)

Methyl ether of the tri methyl dersvative C₂H₂(OMe), CO₂Me (281°) Oil

[102°] Ethyl ether EtA' Colourless crystals (containing aq) melting at 86° when hydrated FeCl, gives a greenish-brown colour hydrated FeCl, gives a greenish-brown colour (Will a Albrecht, B 17, 2100, Schiff, A 245, 40).

Tri-ethyl derivative C,H2(OEt),CO2H [100°] Formed by oxidation of the tri ethyl derivative of daphnetic acid with KMnO, (Will, B 17, 1088, 2099) Silky needles, al sol cold water -BaA'2- AgA' Gives C.H. (OEt), when

Ethyl ether of the tre-ethyl dersvative C.H.2(OEt),CO.Et. Oil Formed by ethylating the acid.

Tri oxy benzoic acid C₀H₂(OH)₃CO₂H. Phloroglucin carboxylic acide Formed by boiling phloroglucin (1 pt) with KHCO_a (4 pts) and water (4 pts) (Will a Albrecht, B 17, 2103, 18, 1323) Colourless crystals (containing aq), sol alcohol and ether Split up by boiling water into CO, and phlorogluoin FeCl, gives a trans nent blue colour Alcohol and HCl yields CO, and the diethyl ether of phloroglucin On heating with POCl, it gives an isomeride of tannin, which is, however, not very astringent and gives no colour with FeCl₃ (Schiff)

Tri methyl derivative? C_sH₂(OMe)₃CO₂H Asaronic deid [144°] (300°) Formed by oxidising asarone with boiling aqueous KMnO, (Butlerow a Rizza, J R 19, 3) Needles On distillation with lime it yields CaH3(OMe)3 (246°)

References -BROMO, BROMO-NITRO, CHLOBO, CHLORO IODO, CHLORO NITRO, IODO, and IODO

NITRO OXY BENZOIC ACIDS

O OXY-BENZOIC ALDEHYDE C,H,O2 C₈H₄(OH) CHO Salvcylic aldehyde Mol w 122 [c -20°] (196 5°) S G 4 11671 (Bruhl) -20°] (196 5°) S G 29 1 1671 (Bruhl) 1 5960 R_{∞} 54 53 Occurs in the blossom of the meadow sweet (Spiraa ulmaria) (Ettling, A 35, 247) and in Crepis fætida (Wicke, A 91,

Formation —1 By oxidation of saligenin or salicin (Piria, A 30, 153) -2 In the products of the dry distillation of quinic acid (Wohler, A 51, 146) -3 By mixing chloroform (15 pts), phenol (10 pts), NaOH (20 pts), and water (35 pts), at 50°, boiling with inverted condenser, distilling off excess of chloroform, acidifying and distilling with steam (Tiemann & Reimer, B 9,

Properties -Liquid, with pleasant odour, v sl sol water, miscible with alcohol and ether Turns red in air Added to 'Vermouth' and other liqueurs Produces epileptic convulsions in dogs (Laborde a Magnan, J Ph [5] 16, 448) FeCl, colours its aqueous solution violet Does not reduce Fehling's solution Combines with KHSO, forming C,H,O(OH)SO,K crystallising

in needles (Bertagnini, A 85, 193)

Reactions—1 Yields o oxy benzoic acid on oxidation -2 Sodium amalgam reduces it to saligenin (Beilstein a Reinecke, A 128, 179) -8 Heated with ZnCl2 and HOAc it forms red amorphous C,4H,0Os, insol water, which dissolves in alkalis with violet red colour but is insol It yields amorphous C₁₄H₉AcO₃ (Bourquin, B 17, 502) -4 Ac2O (2 mols) at 180° forms C₆H₄(OAc) CH(OAc), [100°] which splits up on distillation into Ac₂O and C₆H₄(OAc) CHO (255°) On treatment with soda the compound $C_sH_s(OAc)$ CH(OAc), yields $C_sH_s(OH)$ CH(OAc), [104°] (Barbier, C R 90, 87) —5 Acetyl chloride yields 'disalicyl aldehyde' $C_{14}H_{10}O_s$ [130°] The same body is formed by the action of BzCl, succinyl chloride, and PCl, (Cahours, A 78, 228, Perkin, A 145, 299, Zwenger, A Suppl 8, 42) It crystallises from alcohol in long needles, and to converted by Br in HOAo to C₁.H.Br.₂O₂ [166°], together with C₂.H.Br.₂(OH) OHO [105°] and C₂.H.Br.₂(OH) OHO [88°] (Bradley, B 22, 1134).

Enc. - dust and HOAc form C₁.H.₂O₂ crystallising in needles [82°] (Tiemann, B 19, 857) —7 Browne forms C₁.H.Br.₂(OH) OHO and CH Br. O [Weener 21 [20]48 277). C.H.Br.O (Werner, Bl [2] 46, 277) -8. Cyanogen

bromide forms crystalline C.H.NO. (Cahours, A. 108, 322) -9 Ammonium cyanide and alcohol form $C_{22}H_{18}N_2O_4$ [143°] and $C_{29}H_{21}N_2O_5$ [168°] (Haarmann, B 6, 841) -10 Sodium succinate and acet canhydride form, on heating, dicoumarin C_eH₄<0 CO CO CO C_eH₄ (Fittig, 2523) —11 Theoglycollic acid and zine chloride form C₆H₄(OH) CH(SCH₂ CO₂H)₂ [148°] (Bongartz, B 21, 480) —12 Gaseous or alcoholic ammonia gives rise to 'hydrosalicylamide' C,H,(OH) CH N CH(C,H,OH) N CH C,H, OH which forms yellow crystals [145] (Ettling, A 35, 249, Herrfeld, B 10, 1270) It is insolwater, sl sol cold alcohol, and is decomposed by boiling acids and alkalis into NH, and o oxybenzoic aldehyde It is converted by alcoholic ammonium sulphide into crystalline C21H18N2SO2 and by HOy and HOI into two isomeric crystal-line 'hydrocyansalides' $C_{22}H_{16}N_2O_2$ (Beilstein, A 136, 170) Hydrosalicylamide forms the salts FeC₂₁H₁₅N O₂NH₃ and Cu₃(C₂₁H₁₅N₂O₃)₂2NH₃ — 13 Methylamine gas forms C₆H₄(OH) CH NMe an oil (229°), resolved by acids and alkalis into NH₂Me and salicylic aldehyde (Dennstedt a Zimmermann, B 21, 1553)—14 Ethylamine forms the homologous C₂H₁₁NO (237°)—15 C,H,(OH) CH NPh Aniline forms [50 5°] (Schischkoff, C R 45, 272, Emmerich, A 241, It forms a crystalline compound with p Nitro aniline forms the compound C.H.(NO.) N CH C.H.OH[115°] -16 Dr methylp phenylene damnne forms in like manner C.H.(OH) CH N C.H.NMe₂ [134°] (Nuth, B 18, 573) Di methyl aniline and ZnCl₂ form C.H.(OH) CH(C.H.NMe₂) —17 Benzidine in weak alcoholic solution forms the compound C₁₂H₈[N CH C₆H₄ OH]₂ crystallising from benzene Di amido ditolyl in colourless needles [260°] forms the homologous C₁,H_{1/2}N CH C₆H₁OH)₂ [202°] (Schiff a Vanni, A 258, 374)—18

Ethylene dramine forms C₂H₄(N CH C₆H₁OH)₂ [126°] (Mason, B 20, 271)—19 Ethylene analysis of the control of the con hne forms C₂H₄ (NPh)₂ CH C₆H₄OH [116°] (Moos, B 20, 733) -20 p Tolundine gives rise to C₆H₄Me N CH C₆H₄ OH [100°] (Jaillard, Z 1865, 440) -21 Phenylene m dramine hydrochloride yields C.H.(N CH C.H.OH)2 forming crystalline B'2H2PtCl6 (Schiff, A 253, 329) Tolylene mdiamine yields homologous C,H,(N CH C,H,OH), [109°] -22 Tolylene o dramme forms a compound C₂₈H₂₂N₂O₃ [106°-110°] and azurine C₂₈H₃₂N₄O₃ [250 5°] which exhibits blue fluor escence in alkaline solution (Ladenburg, B 11, 596) -23 (8) Naphthylamine reacts forming C₁₀H,N CH C₆H,OH [121°] (Emmerich, A 241, 351) -24 Urea in aqueous solution gives (NH, CO NH), CH C, H, OH, whence Cu(C₂H₁₁N₄O₂)₂ (Schiff, A 151, 199) — 25 Cu(C₂H₁₁N₄O₂)₂ (Schiff, A 151, 199) — 25 m Amido-bensoic acid forms the compound CO₂H C₂H₄ N CH C₄H₄OH [190°] which forms an amide [186°] (Schiff, A 210, 114) Salts — KC,H₅O₂aq yellow tables S (al-cohol) 5 (Michael, Am 1, 809) — NaHA'₂ aq — Cohol) 5 (Michael, Am 1, 809) — NaHA'₂ aq —

BaA'22aq -Pb(OH)A' -CuA'2 brownish green

Acetyl derivative C.H. (OAc) CHO [37°] (258°) Formed from C₆H₄(ONa) CHO in ether by adding Ac.O (Perkin, A 148, 203, 150, 82) Butyryl dersvative C₁₁H₁₂O₂. 270°). Oil

Bensoyl derivative C.H. (OBz) CHO Oil.

Glucoside v Helicin

Methyl derivative C.H. (OMe) CHO [35°] (238°). Formed from C.H. (ONa) CHO, MeI, and MeOH (Perkin, A 145, 302, C J 55, 550, Voswinckel, B 15, 2024) Thick prisms, nearly insol water, m sol alcohol, v sol ether Alcoholic HCl and H₂S form the (8) throaldehyde C₂₄H₂₄S₃O₃ [224°] While at -10° the (a)- isomeride C₂₄H₂₁S₃O₃ [157°] is formed (Baumann a Fromm, B 24, 1446) Alcohol and colourless ammonium sulphide yield C48H48S6O6 [85°-88°] When KCy followed by HCl is added when key lollowed by Holl sadded to the ethereal solution of C_H₄(OMe) CHO there is formed C₆H₄(OMe) CH(OH) CN [71°] whence alcoholic NH₂ at 70° yields (C₆H₄(OMe) CHCy)₂NH [123°], and alcoholic aniline at 100° gives C₆H₄(OMe) CH(NHPh) CN [61°] (V) Ethylene diamine at 120° forms crys-

talline C.H. (N CH.C.H., OMe),

Ethyl derivative C.H. (OEt) CHO [7°]
(249°) (Göttig, B 10, 8, Perkin, A 145, 306,
C J 55, 551) With alcoholic NH, it yields crystalline N2(CH C6H4 OEt), which is converted by heating at 165° into an amorphous isomeride yielding crystalline B'₂H₂PtCl₆ (Perkin, A 145, 308) Forms with aniline oily C₆H₄(OEt) CH NPh (Schiff, A 150, 195), and with ethyl aniline oily C₆H₄(OEt) CH(NEtPh)₂ Aqueous urea forms

orystalline C₁₁H₁₈N₄O₃ aq
Isobutyl derivative C₅H₄(OC₄H₅) CHO Oil (Baumann a Fromm, B 24, 1448) Alcoholic HCl and H₂S form the (a) [142°] and (β) [163°] isomerides $C_{23}H_{42}S_3O_3$ sulphide yields $C_{44}H_{56}S_5O_4$ [52°-56°] Ammonium

Bensyl derivative C.H. (OC,H.) CHO

Derivatives of o oxy bensoic orth

aldehydeC_sH₄(OH) CH(OAc)₂ [104°] Formed from the aldehyde and Ac₂O at 150° (Perkin, A 146, Tables (from alcohol) C₆H₄(OAc) CH(OAc)₂ [101°] Needles (from alcohol)

C_cH₁(OMe) CH(OAc)₂ [75°] Prisms C_cH₁(OEt) CH(OAc)₂ [89°] Prisms, insol Aq Oxim C_cH₁(OH) CH NOH [57°] White crystals, resolved by warm HClAq into its com ponents (Lach, B 16, 1782, 17, 1572) Ac₂O converts it into acetyl o-oxy benzonitrile compound NHPh CO O C.H. CH NO CO NHPh [115] is formed by phenyl cyanate (Goldschmidt a Schulthess, B 22, 3102) —B'HCl — C.H. (ONa) CH NONa 3aq small pearly scales

Derivatives of the oxim CoH4(OMe) CH NOH [92°] With phenyl oyanate it yields C₆H₄(OMe) CH NO CO NHPh [105°] (Goldschmidt, B 23, 2741)

C.H.(OMe) CH NOMe Oıl

C.H. (OEt) CH NOEt C.H. (OH) CH NOC.H, Oıl

The (a) isomeride [63°] is formed from o oxy benzoic aldehyde and (a) benzyl-hydroxylamine, while the (β) isomeride $[100^{\circ}]$ is obtained by using (β) benzyl-hydroxylamine (Beckmann, B 23, 3819)

Phenyl hydraside C.H. (OH) CH N NHPh. [148°] Colourless needles (from alcohol) (Fischer, B 17, 575, Rossing, B 17, 3003). C_eH₄(OAc) CH N NAcPh [133°], which forms a crystalline dibromide converted by boiling alco hol into CaHaBra(OAc) CH NaHPh [1880], which yields C.H.Br. (OAc) CH N.AcPh [158°] and |

C.H.Br.(OH) CH N.HPh [1480]

m - Oxy - benzoic aldehyde C.H. (OH) CHO [8 1] [104°] (240°) Formed by reduction of m oxy-benzoic acid in acid solution by sodium-Formed by reduction of amalgam (Sandmann, B 14, 969) Obtained also by oxidation and diazotisation from m amidocinnamic acid (Luff, B 22, 294) Prepared from m-nitro-benzoic aldehyde by reduction and treatment of the amido compound with nitrous acid (Tiemann a Ludwig, B 15, 2043) Needles (from water) Excess of Ac. O forms C.H. (OAc) CH(OAc)2 crystallising in plates [76°

Acetyl derivative C.H. (OAc) CHO (263°) Formed from the K salt and Ac. O Oil

Methyl derivative C₆H₄(OMe) CHO (230°) Oxim C₆H₄(OH) CH NOH [87 5°]

silky needles (Clemm, B 24, 826)

Phenyl hydrazide

C_sH₄(OH) CH N₂HPh [131°] Prisms, v sol

alcohol (Rudulph, A 248, 102)

p-Oxy-benzoic aldehyde C_sH₄(OH) CHO[4 1] [115°] Formed by heating its methyl derivative with HClAq at 200° (Bucking, B 9, 527) Prepared, together with the o-isomeride, by the action of chloroform and alkalis on phenol (Tiemann & Reimer, B 9, 824, 10, 63)

Properties - Needles (from water), v sol alcohol and ether Not volatile with steam FeCl, gives a slight violet tint to its aqueous solution Reduces ammoniacal AgNO, With NaHSO, it forms the crystalline compound

C₆H₄(OH) CH(OH)SO₃Na [112°]

Reactions -1 Potash fusion forms p oxybenzoic acid - 2 Sodium amalgam and water reduce it to C₆H₄(OH) CH(OH) CH(OH) C₈H₄(OH) [222°] and the isomeric di-oxy isohydrobenzoin [198°] which forms the crystalline derivative $C_2H_2(OH)_2(C_6H_4OAc)_2$ [192°] (Herzfeld, B 10, $C_6H_1Br_1(OH)$ CHO [181°] and, when in excess, forms $C_6H_2Br_4(O \ CHO)$ (Werner, BL [2] 46, 278) -4Boiling Ac₂O (3 pts) forms C₆H₄(OAc) CH(OAc)₂ [94°] (Tiemann a Herzfeld, B 10, 64, Barbier, CR 90,37)—5 Heating with HOAc and ZnCl₂ forms red amorphous C₁₄H₁₀O₂, which gives a violet solution in alkalis (Bourquin, B 17,503)— 6 Ammonia forms an oily compound -7 Aniline in ethereal solution forms CeH4(OH) CH NPh [191°] -8 p Tolurdine yields the compound C.H. (OH) CH NC,H, [213°] — 9 Di-methylphenylene - dramine gives rise to crystalline C₆H₄(OH) CH NC₆H₄NMe₂ decomposing at 240° (Nuth, B 18, 574) — 10 (8)-Naphthylamine forms C₆H₄(OH) CH NC₁₀H₇ [220°] (Emmerich, A 241, 356)

Acetyl derivative C, H, (OAc) CHO (260°) (Barbier, Bl [2] 33, 52, C R 90, 37), (265°) (T a H) Formed from C.H. (OK) CHO and

Ac₂O Oil

Methyl Methyl derivative C_eH₄(OMe) CHO Anisic aldehyde Mol w 136 (248°) SG 18 1 228 Formed, together with anisic acid, by oxidation of anethol or oil of anise (Cahours, A Ch [3] 14, 484, 23, 354, Rossel, A 151, 25) Formed also by distilling calcium anisate with calcium formate (Piria, A 100, 105) and by methylation of p-oxy-benzoic aldehyde (T a H) Oil, forming with H₂SO₄ a crimson solution, turned violet on heating With NaHSO₄ it forms crystalline C₂H₂NaSO₄ aq (Bertagnini, A. 85,

268) Reactions -1 Alcoholic potash forms the 205) Reactions—I aconomy possess to the state of the corresponding alcohol and acid—2 Alcoholic HCl and H₂S form C₂H₂S₂O₃ [183°] and, at -10°, an isomeride [127°] (Baumann a Fromm, B 24, 1442) Alcoholic H.S forms the through the corresponding to the c B 24, 1442) Alcoholic H.S forms the thio-aldehyde [75°-77°], while alcoholic ammonium sulphide forms a polymeric thioanisic aldehyde $[92^{\circ}]$ and the disulphide $(C_6H_4(OMe) CH_2)_2S_2(B'a)$ F) —3 Sodum amalgam forms two 'hydra nisoins' C₆H₄(OMe) CH(OH) CH(OH) C₆H₄OMe, melting at 172° and 125° (Samosadsky, Z 1867, 678, 1868, 643) Boiling dilute H₂SO₄ converts the isomeride [172] into $C_{18}H_{18}O_3$ [95°] (Rossel, A 151, 36) Zinc and hydrochloric acid form $C_0H_1(OMe)$ CH OH and crystalline $C_{16}H_{18}O_3$ Aqueous HCy (28 p c) forms H(OH)CN [63°], which yields H(OH) CO₂H on saponification [215°] — 4 C₆H₄(OMe) CH(OH)CN C₆H₄(OMe) CH(OH) CO₂H (Tiemann's Friedlander, B 14, 1976) -5 Al coholic KCy yields anisoin—6 Succinic acid yields C_eH₄(OMe) CH CH CH₂ CO₂H and and $C_0H_4(OMe)$ CH OH C(CO₂H) CH $C_0H_4(OMe)$ (Fit tig, B 18, 2523) —7 Di thio glycol gives rise to $C_0H_4(OMe)$ CH S_2 C_2H_4 [65°] (Fasbender, B 21, 1476) -8 Aqueous ammonia produces anishydramide' N (CH C₈H₄OMe), [120°] converted at 170° into crystalline 'anisine' C₂₄H₂₄N₂O₃, which forms the salts B'HCl aq and B',H,PtCl, (Bertagnini, A 88, 128) -9 Ethylene diamine forms C2H4(N CH C6H4OMe), [111°] (Mason, B 20, 272) -10 Aniline gives rise to crystalline 20, 733) – 12 o Tolundure reacts, forming C₆H₄(OMe) CH NPh) – 11 Ethylene annine forms C₆H₄(OMe) CH (NPh)₂ C₂H₄ [164°] (Moos, B 20, 733) – 12 o Tolundure reacts, forming C₆H₄(OMe) CH NC₆H₄Me [32°] The p isomeride [92°] is also crystalline (Steinhart, A 241, 340) — 13 Phenylene - di - methyl - p diamine forms C₆H₄(OMe) CH N C₆H₄NMe [148°] (S, of Nuth, B 18, 574) — 14 Tolylene-o diamine hydro-Toly of the state gives C₅H₄(OMe) CH(NHBz)₂ [192⁻] —18 Urea forms crystalline C₆H₄(OMe) CH(NH CO NH.)₂ and C₁₅H₂₄N₅O₅ —19 Carbanne ether and HCl give C₅H₄(OMe) CH(NH CO NH)₂ (172⁻)

Oxim C₆H₄(OH) CH NOH [65°] from the aldehyde and hydroxylamine (Lach, BWhite needles Converted by Ac,O 16, 1785) AcCl into C₆H₄(OH) CN

CeH, (ONa) CH NONa 3aq

Methyl derivative of the oxim C₆H₄(OMe) CH NOH (a) - Isomeride [62°] Formed from anisic aldehyde and hydroxyl amine (Westenberger, B 16, 2993, Goldschmidt a Polonowska, B 20, 2407, 22, 3102, 23, 2163; Beckmann, B 21, 768, 23, 1687, Miller, B 22, Tastes White plates, m sol hot water 2790) sweet Heated with Ac₂O and HCl it gives C₆H₄(OMe) CN [61°] NaOEt and benzyl chloride yield the (a) benzyl ether [46.5°] Ac₂O forms $C_aH_4(OMe)$ CH NOAc [48°] (Hantzsch, \hat{B} 24, 41), crystallising in prisms Phenyl cyanate forms crystallising in prisms Phenyl cyanate forms C.H. (OMe) CH NO CO NHPh [82°] NaOMe and MeI form C₆H₄(OMe) CH NOMe [43°] (246°) — (β)-Isomeride [130°] Ppd as hydrochloride by passing HCl into an ethereal solution of the Slender needles Has no taste. (a) isomeride With NaOEt and benzyl chloride it yields the (8)-benzyl ether [107°] The acetyl derivative C_eH₄(OMe) CH NOAc [64°] is converted by Na₂CO₃Aq into the intrile [60°]

Phenyl-hydrizide C₃H₄(OH) CH N₂HPh

[178°] Tufts of needles (Rudolph, A 248, 102) Phenyl-hydrazide of the methyl drivative C,H,(OMe) CH N2HPh [121°]

c Di oxy benzoic aldehyde m Methyl derivative C_eH₂(OMe)(OH) CHO [3 2 1] (264°-268) Formed, together with vanilin, by the action of chloroform on a solution of guarscol ın dılute NaOH (Tiemann a Koppe, B 14, 2020) Liquid, volatile with steam, sol alcohol, ether, and benzene, nearly insol water FeCl, colours its alcoholic solution violet

D1 oxy-benzoic aldehyde C_eH₃(OH)₂CHO [4 2 1] (β) Resorcylic aldehyde [135°] Formed by the action of chloroform and NaOHAq on resorcin (Tiemann a Lewy, B 10, 2212) Needles (from water), v sol water, alcohol, and ether FeCl, colours the aqueous solution reddish-

brown Readily resinified

o Methyl derivative C.H. (OH) (OMe) CHO [153°] [4 2 1] Formed, together with the p methyl derivative, by the action of chloroform and NaOH on C.H.(OH)(OMe) [1 3] (Tremann a Parrisius, B 13, 2365) Colourless plates, sl Gives white crystalline pps with I AgNO, and with Pb(OAc), Yields sol, water ammoniacal AgNO, and with Pb(OAc), an acetyl derivative C.H.(OAc)(OMe)CHO [86°]

p Methyl derivative C.H. (OMe) (OH) CHO [4 2 1] [63°] Formed by partial methylation of the aldehyde White plates, nearly insol FeCl₃ colours its alcoholic solution reddish violet Gives pps with ammoniacal

AgNO, and lead acetate

Di-methyl derivative C.H. (OMe)2CHO [68°] Obtained by methylation, and also by oxidation of the di-methyl derivatives of (a) and (3) umbellic acid with $KMnO_4$ (Will, B 16, 2117) Needles (from dilute alcohol)

Di ethyl derivative [72°

Phenyl hydrazide C.H. (OH) CH N.HPh [c 158°] Needles (Rudolph, A 248, 104)

Di-oxy benzoic aldehyde

C₆H₄(OH)₂ CHO [5 2 1] Gentisic aldehyd**e** Formed by boiling hydroquinone with chloroform and aqueous (18 p c) NaOH (Tremann a Muller, B 14, 1986) Flat yellow needles, v sol water Gives a transient blue colour with Yields gentisic acid on fusion with potash Alcoholic aniline forms the anilide C₆H₅(OH)₂CH NPh, crystallising in red needles

m Methyl derivative C₆H₃(OMe)(OH)CHO [5 2 1] [4°] (248°) (H=1) 757 (obs) Formed from methyl hydroquinone CoH4(OH)(OMe) [14], chloroform, and NaOHAq Liquid, volatile with steam, sl sol water Gives a bluish green colour with FeCl. Aniline yields C₆H₃(OMe)(OH)CH NPh [59°], crystallising in red needles The acetyl derivative C_eH₃(OMe)(OAc)CHO [63°] crystallises in needles, and is converted by boiling Ac.O into C_cH_s(OMe)(OAc) CH(OAc)₂

Di methyl derivative C.H. (OMe), CHO. [51°] Volatile with steam Not coloured by FeCl.

m-Ethyl derivative C_eH₂(OEt)(OH)CHO [5 2 1] [52°] (280°) Yellow prisms, nearly insol water Coloured violet by FeCl. [69°], (c 285°) Vol. III Yields C.H.(OEt)(OAc)CHO Di-ethyl derivative C.H.(OEt)2CHO [60°] (c 283°) Needles (T a M. Hantzsch, Needles (T & M , Hantzsch, J pr [2] 22, 468)

Di-oxy-benzoic aldehyde

CaH2(OH)2CHO [4 3 1] v PROTOCATECHUIC ALDE HYDE

Tri-oxy benzoic aldehyde Tri-ethyl derivative C.H. (OEt), CHO [4 3 2 1] [70°] Formed by oxidising the tri ethylderivative of daphnetic acid with KMnO, (Will a Jung, B 17, 1088)

Tri-oxy benzoic aldehyde Tri-ethyl derivative C₆H₂(OEt)₂CHO [95°] Formed by oxidation of the tri-ethyl derivative of (a) or (β) æsculetic acid with alkaline KMnO₄ (Will) B 16, 2112) Large crystals, insol water

Tri oxy benzoic aldehyde Tri-methyl derivative C.H2(OMe)3CHO [114°] Formed by oxidation of asarone (Butlerow a Rizza, J R 19, 3) Needles, v sol hot water

References - Brown, CHLORO, and IODO

OXY BENZOIC ALDEHYDE

m-OXY-BENZOPHENONE C,H, CO C,H,(OH) [116°] Formed by the action of nitrous acid upon m amido-benzophenone (Geigy a Koenigs, B 18, 2402) Needles

p Oxy-benzophenone C.H. CO C.H. OH [14] p-Benzoyl phenol Formed by heating phenol with BzCl and ZnCl₂ (Grucarevitch a Merz, B Obtained also from p amido benzo 6, 1245) phenone by the diazo reaction (Doebner a Weiss, B 14, 1840, A 210, 275) Needles or plates

Acetyl derivative [81°] Needles (from alcohol) (Doebner a Stackmann, B 10, 1970)

Benzoyl derivative [113°]

thyl derivative C.H. CO C.H.OMe Four sided prisms (Rennie, C J 41, Methyl derivative 227) Possesses two oxims CaH, C(NOH) CaH, OMe, a stable oxim [116°] yielding B'HCl, an acetyl derivative [53°], and a benzyl ether [74°], and an unstable oxim [140°], which yields B'HCl [124°], an acetyl derivative [135°], and a benzyl ether [60 5°] (Schafer, A 264, 158, Hantzsch, B 24,

Ethyl derivative C₆H₃CO C₆H₄OEt [39°] (above 300°) Formed from C₆H₃OEt, benzoyl chloride, and AlCl, (Gattermann, Ehr

hardt, a Marsch, B 23, 1206)

Discount benzophenone CO(C,H,OH), [60°] Formed by heating diphenylene ketone oxide with alcoholic potash at 180° (Richter, J pr [2] 28, 273, Graebe a Feer, B Prisms or plates (from ligroin) 19, 2607) yellow crystals (from alcohol) -K.A" KĤA" crystals, v e sol water

Acetyl derivative C13H8Ac2O3 (G a F), [83°] (R) Prisms (from alcohol)

Bensoyl derivative C₁₃H₂Bz₂O₃ [104°] Methyl derivative C₁₃H₂MeO₃ [69°]

Di-methyl derivative C₁₁H₁₈Me₃O₁ [98°] (R), [104°] (G a F) Prisms Forms the oxim C(NOH)(C₆H₁ OMe), [188°] Di-ethyl ether C₁₃H₂Et₂O₁ [109°] Needles (from dilute alcohol) Yields the

phenyl hydrazide C(N2HPh)(C6H4OEt), [114°] Oxim C(NOH)(O,H,OH),

Phenyl-hydraside C(N.HPh)(C.H.OH).

[152°]

op-D1-oxy-benzophenone [2 1] C.H.(OH) CO C.H.(OH) [1 4] [144°] Formed by heating salicylic acid with phenol ÝΥ

and SnCl, at 120° (Michael, B. 14, 656, Am 5, | 83) Large yellow plates, al sol water - Ag.A"aq [889] Acetyl derivative C18H.Ac2O.

D1-p-oxy-benzophenone CO(C'H'OH)*

[2100]

From CH₂(C₆H₄OBz)₂ by Formation -1oxidation and saponification (Gail, A 194, 834) 2 By fusing phenol-phthalein with potash (Baeyer a Burkhardt, B 11, 1299, A 202, 126). 3 By heating aurin with water at 240° (Caro a. Graebe, B 11, 1348), or rosaniline with water at 270° (Liebermann, B 6, 951, 11, 1435) — By the action of HNO, on dipamidobenzophenone (Staedel a Sauer, B. 11, 1747)

Properties —Long needles, m sol hot water

On treatment with PCl, followed by phenol and H2SO41t yields aurin Bromine forms C13H6Br4O2

[2149]

49]
Acetyl derivative C₁₃H₈Ao_.O_{.s} [148°].
Bensoyl derivative C₁₄H₈B₂O_{.s} [182°].
Methyl derivative C₁₅H₈Me₂O_{.s} [144°].
Addiss (Bosler, B 14, 328) Yields C₁₅H₁₅Br₂O_{.s} Needles (Bosler, B 14, 328) [181°] and an oxim [133°]

Ethyl derivative C₁₃H₂EtO₂ [14
Di-ethyl derivative C₁₃H₂Et₂O₃
(Gail), [131°] (Gattermann, B 22, 1131)
(B) Di-exy-benzophenone C₁₄H₁₆O₃ [147°]

Formed from di nitro benzophenone [149°] by reduction and application of the diazo reaction (Staedel a Sauer, B 18, 836) Needles

Acetyl derivative C13H8Ac2O3 [90°] Benzoyl derivative C, H, Bz₂O [1020] D1-oxy-benzophenone C₆H₅CO C₆H₃(OH)₂ [145°] Formed from di benzoyl pyrocatechin, BzCl, and ZnCl₂ (Doebner, A 210, 261) Needles

(containing | aq)
Benzoyl derivative C13H3Bz2O3 C.H. CO C.H. (OH) Di oxy benzophenone Benzoresorcin [144°] Formed from resorcin, BzCl, and ZnCl at 120° (Doebner a Stachmann, B 11, 2270) Needles, sol hot water

Benzoul derivative C13H8Bz2O3 [141°]

Tri oxy benzophenone

C₆H₄(OH) CO C₆H₃(OH), [1 2 4] [133°] Formed by heating salicylic acid with resorcin at 200° (Michael, B 14, 658), or by heating oxy diphenylene ketone oxide with NaOH at 270° (Graebe, A 254, 291) Plates, sl sol water

Tetra-oxy-benzophenone $CO(C_6H_4(OH)_2[1\ 2\ 5])_2$ [202°] is Eukanthonic

ACID(q v)

Hexa-oxy-benzophenone $CO(C_0H_4(OH)_3)_{2^*}$ Anhydride C, H,O, Anhydropyrogalloketone Formed by fusing gallein with alkalis (Buchka, A 209, 270) Brown powder

Acetyl derivative C13HACO [237°]

OXY-BENZOPHENONE O-CARBOXY-LIC ACID Methyl derivative C15H12O4 1e C_cH₄(OMe) CO C_cH₄ CO₂H Anisole phthalore acid [148°] Formed by the action of phthalo anhydride (50 g) on anisole (150 g) in presence of AlCl, (80 g) (Nourisson, B 19, 2103) Colour-less crystals (from toluene) Split up by potashfusion into benzoic and p-oxy benzoic acids Yields a bromo- derivative [196] Cone H.SO. Cone H2SO4 forms m oxy-anthraquinone Distillation with zinc dust gives antiracene —NaA' —KHA', CaA', 2aq —BaA', 4aq white needles —AgA'. Di oxy bensophenone carboxylic acid

C.H. (OH), CO C.H. CO.H. [200°]. Got by fusing

fluorescein with NaOHAq (Baeyer, A 183, 23) Crystals (containing aq)

DI-OXY-BENZOPHENDNE SULPHONIC ' ACID C₆H₅(OH)₂.CO C₆H₄SO₅H Formed by heating O₆H₄(SO₂NH₄)CO₂H with resorcin (Remsen, Am 9, 5, 372, 11, 73) Small plates (containing 2aq) —BaA"—NH₄HA" heating

OXY-BENZOYL ACETIC ACID C,H,O, 10 C_eH_s CO CH(OH) CO₂H [125°] Formed from nitroso benzoyl-acetic ether Bz C(NOH) CO₂Et and NaOHAq (Baeyer a Perkin, B 16, 2133, C J 47,245) Small prisms (from water) -AgA'

OXY-BENZOYL BROMIDE Methyl deri vative C.H. (OMe) COBr Formed from anisic aldehyde by cautious treatment with bromine (Cahours, A. Ch. [3] 14, 486) Silky crystals, resolved by KOHAq into potassium anisate and potassium bromide

p-OXY-BENZOYL CHLORIDE Methyl derivative C.H. (OMe) COCI (262°) 8 G 15 1 261 Formed from anisic acid and PCl, (Cahours, A Ch [3] 23, 351) Oil, converted by

water into anisic acid

p OXY BENZURIC ACID C.H.NO. C₆H₄(OH) CO NH CH₂ CO₂H [c 228°] Occurs in the urine of dogs to which p oxy benzoic acid or hydro p coumaric acid has been administered (Baumann a Herter, H 1, 260, Schotten, H 7, 26) Prisms, m sol water

OXY DIBENZYL v OXY DI PHENYL ETHANE C,H₈O₂ 2 c 124 O OXY-BENZYL ALCOHOL C₆H₄(OH) CH₂OH Saligenin [82°] S 7 at 22° S (benze S (benzene) 19 at 18° Formed by the hydrolysis of salicin (Piria, A 56, 37), by reducing o oxy benzoic aldehyde with sodium amalgam (Beilstein, A 128, 179), and by heating phenol with CH₂Cl. and aqueous NAOH at 100° (Greene, Am 2, 19) Tables, v e sol hot water FeCl, gives a blue colour Dilute H_2SO_4 forms saliretin $C_{14}H_{14}O_8$ or $C_{28}H_{26}O_5$, a yellowish powder, insol water (Gerhardt, A Ch [3] 7, 215, Beilstein, A 117, 84, Kraut, A 156, On heating with glycerin at 100° it forms saliretone C14H12O3 [1215°] crystallising from water (Giacosa, J pr [2] 21, 221)

Methyl derivative CoH4(OMe) CH2OH (248°) SG 23 1 120 (Cannizzaro a Korner, B 5, 436)

Ethylderivative CaH4(OEt) CH2OH (265°) Solidifies at 0° (Botsch, M 1, 621)

m Oxy-benzyl alcohol [3 1]C₈H₄(OH) CH OH [67°] (c 300°) A product of the action of sodium-amalgam on m oxy benzoic acid in acid solution (Van der Velden, J pr [2] 15, 163) White mass, v sol hot water FeCl₃ gives a violet colour

Acatyl derivative C.H.(OH) CH.OAc [55°] (295°-802°) Crystalline, v sl sol water Dr acetyl derivative C.H. (OAc) CH2OAc (c 290°). Oil, sol alcohol and ether

p Oxy-benzyl alcohol C₆H₄(OH) CH₂ OH [110°] Prepared by slowly adding 40 pts of 8 pc sodium amalgam to a solution of 1 pt para-oxy benzaldehyde in 10 pts water and 5 pts alcohol, kept slightly acid with H2SO4 (Biedermann, B. 19, 2378). Thin white needles ' V. sol water, alcohol, and ether, sl sol benzene and chloroform, nearly insol ligroin in conc H.SO, with a splendid violet colour.

Mono-acetyl derivative

C.H.(OH) CH2 OA? [84°], small yellowish needles, v sol al ohol and ether, sl sol water Di acety l derivative

 $C_0H_4(OAc)$ CH_2 OAc [75°], small needles, \blacktriangledown . sol alcohol and ether, nearly insol water

Methyl derivative C.H. (OMe) CH2OH Anisic alcohol Mol w 138 [45°] Formed, together with anisic acid, by mixing anisic aldehyde with alcoholic potash (Cannizzaro a Bertagnini, A 98, 188, 137, 246, G 2, 61) Ob tained also by methylation (Biedermann, B 19, C₆H₄(OMe) CH₂OMe (226°)

D1-oxy benzyl alcohol

Ethyl derivative

CH (OM) CH (OM) CH (OM)

D1-oxy benzyl alcohol

Ethyl derivative

C₆H₂(OEt)(OH) CH₂OH [5 2 1] [84°] Formed by adding 5 pc sodium amalgam to the corresponding aldehyde suspended in water The product is acidified and shaken with ether (Hantzsch, J pr [2] 22, 475) Large thick tablets, changing at 100° into a brown amorph-

ous mass Acids also resinify it

D1 oxy-benzyl alcohol C₆H₃(OH)₂ CH₂OH [431] Methyl derivative C₈H₁₀O₄ re C₈H₁(OH)(OMe) CH₂OH[431] Vanilyl alcohol [115°] Formed by the action of sodium-amalgam on vanillin (Tiemann, B 8, 1125, 9, Formed also by the action of emulsin on the glucoside $C_6H_3(OC_6H_{11}O_5)(OMe)CH_2OH$ [120°], a crystalline body (containing aq) prepared by reduction of glucosyl vanillin (Tiemann B 18, 1595) Prisms, v sol alcohol

Methylene derivative C.H. (O.CH.) CH.OH Prperonyl alcohol [51°]. Got by reducing piperonal CoH3(O2CH2) CHO with sodium amalgam and hot water (Fittig a Remsen, A 159, 138) Long crystals, m sol hot water

Reference - CHLORO OXY BENZYL ALCOHOL

O OXY BENZYL AMINE C.H. (OH) CH2NH2 Formed by heating its methyl deriva 「125°ໄ tive with HClAq at 150° (Goldschmidt a Ernst, B 23, 2744) and by the action of dilute H SO and zinc dust on C6H4(OH) CH N NH C6H4CO H (Tiemann, B 23, 3017) Groups of white needles (from ether) Readily sublimes Ferric chloride colours its solution deep violet blue—B'HCl—B'HCl—B'HCl, 2aq [197°] Golden needles

Acetyl derivative C,H,(OH) CH, NHAc

[140°] Colourless needles, sol alkalis

Methyl derivative C,H,(OMe) CH, NH,
[294°] A 704 mm.

(224° at 724 mm) Formed by reducing the oxim C₀H₄(OMe) CH NOH in alcoholic solution Formed by reducing the with sodium amalgam and HOAc (Goldschmidt a Ernst, B 28, 2742) Liquid, v sol water Yields C,H,(OMe) CH, NHAc [97°]—B'HCl [150°]—B',H,PtCl, 2aq [187°] Golden plates

p Oxy benzylamine

[95°] Formal C₆H₄(OH) CH₂ NH₂ aq Formed from p amido benzylamine,

NaNO₂, and HCl (Salkowski, B 22, 2143).

Plates — B'HCl — B'₂H_PtCl₂2aq flat needles

Methyl derivative C₆H₄(OMe) CH NH₂.

(222°) (S), (235°) (G a P) Formed by reducing hydroanisamide in alcoholic solution with sodium amalgam (Steinhart, A 241, 835) Obtained also by reduction from the oxim C.H. (OMe) CH NOH (Goldschmidt a Polonowska, B 20, 2407) Liquid, sol water, volatile with steam—B'HCl. [280°]—B'HHgCl, aq [200°]. Scales —B'.H.PtČl. [210°]

yellow needles Absorbs CO, from the air, forming a compound crystallising in needles [110°] (cf Cannizzaro, A 117, 240)

Acetyl derivative C.H. (OMe) CH, NHAc.

[96°

Di-o-oxy di-benzyl amine NH(CH2,C4H4OH)2. [170°] Formed by reducing hydrosalicylamide in alcoholic solution with sodium amalgam (Emmerich, A 241, 349) Needles, v sl sol water Gives an oily nitrosamine—B'₂H₂PtCl₆

Di-methylDi p-oxy di-benzyl amine (C₈H₄(OMe) CH₂),NH derivative Formed by the action of C.H. (OMe) CH_Cl on alcoholic ammonia, and also by $(C_8H_4(OMe)\ OH)_3N_2$. White needles reducing Yıelda a $(C_6H_4(OMe) CH)_8N_2$. White needles Yields a nitrosamine [80°] —B'HCl [243°]. Flat prisms. -B'2H2PtOl, 2aq

o OXY BENZYL-ANILINE

C₀H₄(OH) CH₂NPhH Phenyl-w amido cresol. [106°] Formed by reducing o oxybenzylideneaniline with sodium amalgam (Emmerich, A 241, 344) Needles or plates, sl sol water nitrosamine is oily -B'HCl [131°] -B'2H2PtCl. [184°] M solawater

[208°] p-0xy benzyl aniline Formed in

like manner (E) White needles —B',H.PtCl.

Methyl derivative C.H.(OMe) CH,NHPh.

[65°] Formed by reducing C.H.(OMe) CH NPh
(Steinhart. A 241 227) (Steinhart, A 241, 337) Prisms Gives a nitros amine [104°] -B'HCl [163°] -B'2H2PtCl

DI OXY DI BENZYL BENZENE

C_eH₄(CHPh OH), [171°] Formed by reducing C.H. (COPh)2 with sodium amalgam (Wehnen, B Satiny needles (from dilute alcohol) 9, 310) Yields $C_{20}H_{19}AcO_2$ [97°] and $C_{20}H_{18}Ac_2O_2$ [144°]

OXY O BENZYL BENZOIC ACID C14H12O2 2.6. C₆H₅ CH(OH) C₆H₄ CO₂H Benzhydryl carboxylic acid -KA' amorphous -BaA'2. From the anhydride and baryta

Anhydride C,H, CH< CH CO

Formed by reducing o benzoyl benzoic acid with zinc and HCl (Rotering, J 1875, 596) insoluble powder

Exo Oxy m-benzyl-benzoic acid 「121°T Formed by reducing m benzoyl benzoic acid with sodium amalgam (Senff, A 220, 242) Sating needles in hemispherical groups (from hot water).
Reduced by HIAq (127°) at 170° to m benzylbenzoic acid —NaA' 4aq —CaA', 5aq —AgA' aq
Oxy-p benzyl-benzoic acid [165°] Formed

by reducing p benzoyl benzoic acid (Zincke, A.
161, 102) Needles (from hot water) — NH,A' —
NaA' — KA' — CaA'₂ 5aq — BaA'₂ — AgA' pp

Methyl ether MeA' [110°] Prisms

Oil Ethyl ether EtA'

Oxy bensyl-benzoic acid

C₆H₃ CH₂ C₆H₃(OH) CO.H [140°] Formed from benzyl phenol, sodium, and CO₂ (Paterno a. Fileti, G 3, 237) Needles (from water), sl sol. hot water —AgA' curdy pp, sl sol hot water

DI-OXY BENZYL ETHYL KETONE CARB-OXYLIC ACID Methylene derivative C.H.(O.CH.) CH. CO.H. CO.H. Properoketonic acid [84°] Formed by heating di bromopiperhydronic soid with aqueous Na.CO. (Weinderstein acid acid with aqueous Na.CO. (Weinderstein acid with aqueous Na.CO.) stein, A 227, 38) Silky needles (from CS2) — CaA',—AgA' flocculent pp
OXY-BENZYLIDENE-ACETONAMINE 2.

ACETONAMINE

o-OXY-BENZYLIDENE-m-AMIDO-BENZOIC ACID C.H.(OH) CH N C.H.CO.H [190°] Formed from salicylic aldehyde and aqueous m amido-benzoic acid (Schiff, A 210, 114)

Yellowish needles, v e sol alcohol

Amede C₁₄H₁₂N₂O₂ [186°] Converted by boiling benzoic aldehyde into crystalline C₁₁H₂N₁O₂ whence Ac₂O yields C₁₂H₂₂Ac₂N₁O₄ [220°] The glucosyl derivative of the amide C₂H₁₁O₂O C₂H₄ CH N C₂H₄ CONH₂ [113°] is formed by the action of helicin on mamidobenzamide

D1-oxy-benzylidene-o-amido-benzoic acid C.H.(OH) CH N C.H.(OH) CO.H [5 2 1] [245°] Formed from oxy amido benzoic acid and sali-cylic aldehyde Needles, v e sol alcohol

DI-OXY-BENZYLIDENE DI-AMIDO-DI-PHENYL C₁₂H₆[N CH C₆H₄OH]₂ [145°] Formed from di-o amido-diphenyl and salicylic aldehyde (Reuland, B 22, 3012) Yellow plates

o OXY-BENZYLIDENE-ANILINE C,H,(OH) CH NPh [51°] OXY-BENZOIC ALDEHYDE The p isomeride melts at 191°

OXY-BENZYLIDENE ANTHRONE Ethulether C_eH₄ COCCPh OEt) C_eH₄ [173°]

Formed from bromo benzylidene anthrone and NaOEt (Bach, B 23, 2529) Yellow plates, v sol ether

OXY - BENZYLIDENE - DICARBAMIC ETHER Methyl derivative $C_{14}H_{20}N_{2}O_{5}$ is $C_{6}H_{4}(OMe)$ CH(NH $CO_{2}Et)_{2}$ [172°] Formed from anisic aldehyde and carbamic ether (Bischoff, B 7, 1078) Needles (from dil alcohol)

DI -o- OXY - BENZYLIDENE - ETHYLENE -DIAMINE C16H16N2O2 & C2H4(N CH C6H4OH)2. [126] Formed from ethylene diamine and o oxybenzoic aldehyde (Mason, B 20, 271) The dimethyl derivative [c 113°] and its p isomeride $C_2H_4(N \text{ CH } C_6H_4 \text{ OMe}[1 \text{ 4}])_2[111^\circ]$ are both crys talline

o-OXY-BENZYLIDENE-MALONIC Methyl derivative C₆H₄(OMe)CH C(CO H)₂ [178°] Formed by heating a mixture of maionic acid, $C_0H_0(OMe)$ CHO, and HOAc at 100° (Stuart, C_0J_0 53, 142)

OXY-BENZYLIDENE NAPHTHYLAMINE The o [121°] and p CoH (OH) CH NC 10H, [220°] compounds are formed from (\$\beta\$) naphthylamine and the corresponding oxy benzoic aldehydes (Emmerich, A 241, 350)

o-OXY-BENZYLIDENE DITHIOGLYCOLLIC $C_0H_4(OH) CH(S CH_2 CO_2H)_2$. [148°] Formed from o-oxy-benzoic aldehyde, thioglycollic acid, and ZnCl₂ (Bongartz, B 21, 478)

o OXY-BENZYLIDENE p TOLUIDINE C.H. (OH) CH NC,H, [100°] (Jaillard, J 1865, 428, v OXY-BENZOIC ALDEHYDE)

OXY BENZYLIDENE DI UREA C.H. (OH) CH(NH.CO NH2), v o-OXY-BENZOIC ALDEHYDE

OXY-BENZYL-MALONIC ACID Ethyl derivative C.H. CH(OEt) CH(CO2H)2 120°]. Formed from benzylidene malonic acid and cold alcoholic KOH (Claisen a Crismer, A 218, 141) Crystalline. Split up at 120° into alcohol and benzylidene malonic acid [192°] -KA" -Ag.A"

Isomeride . BENZYL-TARTHONIC ACID

OXY BENZYL-METHYL-ETHYL-PYRIMID.

 $CH_2Ph\ C{\gtrless}_N^N\ {}_{C(OH)}^{CMe}\ >\!\!\!\!\!> CEt$ INE **በ193** 5ግ. Formed from phenyl acetamidine hydrochloride, ethyl-acetoacetic ether, dilute (10 pc) NaOH, and alcohol (Pinner, B 22, 1623) Needles, m. sol water, v e sol alcohol

Di-oxy-bensyl methyl-ethyl pyrimidine

CH(OH)Ph C < N C(OH) > CEt[148°-152°]. Formed from oxy phenyl acetamidine, aceto-acetic ether, and NaOHAq (Pinner, B 23, 2951) OXY BENZYL METHYL-PYRIMIDINE

 $CH_2Ph C < N C(OH) CH$ [175°] from phenyl acetamidine, acetoacetic ether, alcohol, and dilute (10 pc) NaOH (Pinner, B 22, 1622) Prisms, m sol hot water

Oxy-benzyl-di methyl pyrimidine

 $CH_{2}Ph\ C{\stackrel{N}{<}_{N}}\ C(OH){\stackrel{CMe}{>}}CMe$ [181°] Formed from phenyl acetamidine, methyl acetoacetic ether, and NaOHAq (P) M sol water

Oxy-di-benzyl methyl-pyrimidine

CH.Ph C N CMe COH, Ph [192°]. Formed from phenyl acetamidine, benzyl acetoacetic ether, and NaOHAq (P) Needles, insol_water benzyl acetoacetic Di-oxy-benzyl-methyl-pyrimidine C₁₂H₁₂N₂O₂

CH(OH)Ph O N CMe Formed from oxy-phenyl acetamidine, NaOHAq and aceto acetic ether in the cold (Pinner, B 23, 2949) Long needles, v sl sol. water, alcohol, sol acids and alkalis - B'HCl [217°] Needles —B'C,]
AgC₁₂H₁₁N₂O₂ white pp
Acetyl derivative Needles —B'C₆H₂(NO₂)₃OH. [175°]

Yields AgC14H13N2O3, by boiling with Ac₂O B'HCl [188°], and B'C₆H₂(NO₂), OH [160°]

 $C_{12}H_{11}BzN_2O_2$ derivative Benzoyl[205°-208°] —B'HCl [240°] From the base

Di-oxy-benzyl methyl pyrimidine Got from potassium methyl-uracil and benzyl chloride (Hagen, A 244, 1)

Di-oxy benzyl-di methyl pyrimidine

CH(OH)Ph C < N C(OH) > CMe [155°] Formed from oxy phenyl-acetamidine, NaOHAq, and methyl-acetoacetic ether (Pinner, B 23, 2951) -

B'HOAc needles — $AgC_{13}H_{13}N_2O_2$ white pp OXY - BENZYL - (β) NAPHTHYLAMINE The following compounds have been prepared by reducing the products of the action of (β) naphthylamine on the corresponding aldehydes (Steinhart, A 241, 341, Emmerich, A 241,

1 2]C₆H₄(OH) CH₂NHC₁₀H, [147°] —B'HCl T188

[1 2]C₆H₄(OH) CH₂ N(NO)C₁₆H₄. [165°] [1 2]C₆H₄(OMe) CH₂ NH C₁₆H₄. [92°] (223°) [1 4]C₆H₄(OH) CH₂ NHC₁₆H₄. [117°] [1 4]C₆H₄(OH) CH₂ N(NO) C₁₆H₄. [142°] [1 4]C₆H₄(OMe) CH₂ NHO₁₆H₄. [101°] —B'HGL

[195°] -B'2H.PtCl, -Nitrosamine

C_eH₄(OMe) CH₂ N(NO) C_{1e}H, [133°] OXY-BENZYL-ISOPHTHALIC ACID Benshydryl-isophthalic acid Anhydride

C_eH_s CH<0.4 (CO₂H_s). [207°]. Formed by the action of zinh and HClAq on benzoyl isophthalic acid (Zincke, B 9, 1763) Needles (from dilute alcohol)—BaA', 2½aq—AgA' pulverulent pp.—EtA' [115°] An isomeric acid, obtained by reduction of benzoyl terephthalic acid, forms $Ca(C_{18}H_{9}O_{4})_{2}$ 8aq (Weber, J 1878,

p-OXY-BENZYL-PHTHALIMIDINE C₆H₄<CH₂>N C₇H₆OH or

C.H. C.H.OH. O. [187°-198°].

Formed from the amido compound by the diazo reaction (Hafner, B 23, 344) Red needles Converted by conc HClAq at 150° into a base C,H,NO

OXY BENZYL PYRIDINE TETRAHYDRIDE

 $C,H,CH < CO NH \\ CH_2 CH_2 > CH_2$ (B)-Benzyl piper [118°] Formed by distilling 8 amido abenzyl valeric acid (Aschan, B 23, 3696) Pearly plates (from hot water) B'C₆H₂(NO₂)₃OH Crystals, sl sol water [97°]

Nitrosamine C₁₂H₁₄(NO)NO [62 5°] OXY BENZYL PYRIMIDINE CARBOXYLIC

 $CH_{2}Ph C < N C(OH) CH$ [230°]

Formed from phenyl acetamidne, oxalacetic ether, and (10 pc) NaOHAq (Pinner, B 22, 1627) Prisma, v sl sol water

OXY BENZYL PYROTARTARIC ACID C₆H₅ CH(OH) CH(CO₂H) CHMe CO₂H Phenylhomortamalic acid Formed from benzoic aldehyde, sodium pyrotartrate, and Ac2O at 125° (Penfield, A 216, 119, Fittig a Liebmann, A The acid splits up, at the moment 255, 257) of liberation, into water and anhydride -

CaC₁.H₁,O₅ 3aq —BaA' 2aq —Ag,A''

An hydride C₁₂H₁₂O₅ Phenylhomopar

conic acid [177°] Plates (from water) Phenylhomopara-AgC₁₂H₁₁O₄ crystals, m sol water—BaA" aq.
—CaA"

Isomeride

 C_eH , CH(OH) $CMe(CO_eH)$ CH_2 CO_2H Formed together with the preceding acid Its salt $BaC_{12}H_{12}O_s$ is got by heating the anhydride with baryta water

18 got by neating the analysis of CHPh $\langle CMe(CO_2H) \rangle$ Anhydride CHPh $\langle CMe(CO_2H) \rangle$ (124 5°) Yields Ba(C₁₂H₁₁O₄)₂, CaA'₂ 2aq, and AgA'

DI - OXY - BENZYL - QUINOLINE CARB-OXYLIC ACID Ethyl derivative

 $C_{\bullet}H_{\bullet} < N C(OEt)$ [147°] Formed by reducing benzyl o nitro benzoyl malonic ether (Bischoff, B 22, 386)

OXY BENZYL SUCCINIC ACID C₁₁H₁₂O₅ te PhCH(OH) CH(CO₂H) CH₂CO₂H Its salts are formed by warming the anhydride with bases — CaC₁₁H₁₀O₃—BaA" 2aq —Ag₂A".

Ethyl ether

CHPh(OH) CH(CO2Et) CH2CO2H Oil $C_{c}H_{s}CH< CH(CO_{c}H)> CH_{s}$ Anhydride

[99°] Phenyl-paraconic acid Formed by heating sodium succinate with benzoic aldehyde and Ac.O (Fittig a Jayne, A 216, 108, 256, 63) Needles (from water), converted by NaOEt into [6] 16, 58).

phenylitaconic acid. Yields Ca(C,H,O4), 2aq, BaA', Saq, and AgA', and the ether EtA' (252° at 25 mm)

p OXY-BENZYL-THIOCARBIMIDE

C.H. (OH) CH.NCS From p oxy benzylamine, CS₂, and HgCl₂ (Salkowski, B 22, 2144) Liquid,

p-OXY BENZYL-THIO-UREA Methyl de-rivative C.H. (OMe) CH, NH CS NH, [95°] (Goldschmidt a Polonowska, B 20, 2409)

Di oxy di benzyl-thio urea Di methyl derivative (C.H. (OMe) CH2NH) CS [150°]

o OXY BENZYL p TOLUIDINE C1.4H13NO 2 e C6H4(OH) CH2NH C6H4Me [116°] Formed by reducing o oxy benzylidine p toluidine in alcoholic solution with sodium amalgam (Emmerich, A 241, 346) Crystals Yields the methyl derivative C₆H_{*}(OMe) CH₂ NHC₆H_{*}Me [110°] and a tetra nitro derivative [168°]—B'HCl [147°]— B'2H2PtCl reddish yellow needles

p Oxy benzyl p toluidine [186°] Yields B'_2H_PtCl_and C_4H_(OMe) CH_NHC_4H_Me [68°], whence B'HCl [160°], B'_2H_PtCl_and the nitrosample CH_OME_6H_ME amine $C_6H_4(OMe)$ CH_2 N(NO) C_6H_4Me [108°]

p Oxy benzyl o toluidine Methyl derivative [55°] Triangular plates (Steinhart, A 241, 340) Yields an oily nitrosamine

o - **OXY** - **BENZYL** - **UREA** $C_0H_{10}N_2O_2$ **6.e** $C_4H_4(OH)$ CH_2 NH CO NH_2 $[170^\circ]$ Formed by warming o oxy benzylamine hydrochloride with potassium cyanate (Goldschmidt a Ernst, B 23. 2745) Prisms, v sol hot water

Methyl derivative

C₈H₄(OMe) CH₂NH CO NH₂ [127°].

p Oxy benzyl-urea Methyl derivative [167°] Needles (Goldschmidt a Polonowaka, B 20, 2409)

δ OXY α BENZYL-VALERIC ACID CH₂(OH) CH₂ CH₂ CH(CH₂Ph) CO₂H Formed from nitroso oxy benzyl pyridine tetrahydride and NaOHAq (Aschan, \hat{B} 23, 3697). Liquid, m sol hot water

 γ Oxy β -benzyl-valeric acid CH, CH(OH) CH(CH,Ph) CH, CO,H Formed by carefully adding dilute HCl to its Ca salt obtained from the lactone (Erdmann, A 254, 217) Prisms (containing aq) Melts at 56° when hydrated HClAq converts it into the lactone. -Ca(C₁₂H₁₅O₂)₂ 4aq -CaA'₂ 6aq

Lactone CH₃ CH CH(CH,Ph) Got by reducing benzyl acetyl propionic acid [99°] with sodium amalgam, and boiling the product with dilute H2SO. Large crystals

DI - OXY - BUTANE CH₂(OH) CHEt(OH) n-Butylene glycol Mol w 90 (192°) S G 8 1 0189 Obtained from wa-di-bromo-n-butane by boiling with baryta water (Grabowsky a Saytzeff, A 179, 325). Liquid, v sol water. Mol w 90 (192°) Yields glycollic and glyoxylic acids on oxidation

Di-oxy-butane C,H,004 t e CH,(OH) CMe2OH Isobutylene glycol (178°) S G 2 1 129 Formed from the bromide and K,CO2Aq (Nevolé, C R 88, 65, 146) and by the action of HClAq on isobutyl alcohol (Lwoff, Bl [2] 43, 112) Formed also in the alcoholic fermentation of sugar (Henninger a Sanson, C R 95, 94, 106, 208) Does not form an acetal with aldehyde (Lochert, A Ch.

Di-oxy-butane CHMe(OH) CHMe(OH) (184°) Formed by heating s-butylene oxide with water at 100° (Eltekoff, J R 14, 872) Liquid

at 100° (Eltekoff, J R 14, 872) Liquid Di-oxy-butane OHMe(OH) OH, CH₂OH (\$)-Butylene glycol. (207°) S G 2 1 0259 Formed by reduction of a dilute, slightly acid, solution of aldol by sodium-amalgam (Kekulé, B 5, 56, A 162, 810, Wurtz, C R 97, 473) Thick Ac₂O at 100° forms liquid, miscible with water C,H,(OAc), (207°) C,H,L, S G 2 2 291 SG 21055 HIAq yields

Di-oxy-butane C₄H₅(OH)₂ (184°) S G 2 1 048 Obtained, vid C₄H₅(OAc)₂ (c 200°), from the crude C₄H₅Br₂ got from fusel oil (Wurts, A Ch. [3] 55, 452) Liquid, miscible

with water

Di-oxy-butane CH₂(OH) CH₂.CH₂ CH₂(OH) Tetramethylene glycol (204°) SG 1011 Formed by the action of dilute H₂SO₄ on tetramethylene dinitramine C.H. (NH NO2), (Dekkers, R. T O 9, 101)

Tri-oxy-butane

CH, CH(OH) CH(OH) CH₂(OH) Butenylgly-cerm (178° at 27 mm) Formed from crotonic aldehyde by reduction, addition of bromine, and boiling the resulting CH, CHBr CHBr CH,OH with water (Lieben a Zeisel, M 1, 832) Thick hquid with sweet taste Ac2O yields C4H, (OAc), Yields $C_4H_7(OH)_2Cl$, $C_4H_7(OH)Cl_2$, and **C₄H,OCl** (Zikes, M 6, 848)

Tri-oxy-butane C,H10O, (240° at 18 mm) Formed from isobutyl iodide by chlorinating and heating the resulting tri-chloro butane with water at 170° (Prunier, Bl [2] 42, 261, C. R 193) Yields nearly solid C,H,(OAc), Tetra-oxy-butane v ERYTHRITE

OXY - BUTANE TRICARBOXYLIC ACID $CMe(OH)(CO_2H) CH(CO_2H) CH_2CO_2H$

Lactions C,H,O, Formed by heating scetosuccinic ether with KCy and HCl (Rach, A 234, 35) At 180° it yields pyrocinchonic anhydride — BaA". — CaA" — Ca₂(C₁H,O₂)₂ — Ba₃(C,H,O,)2.

Di-oxy-butane tetra-carboxylic ether CH(CO₂Et)₂·CH(OH) CH(OH) OH(CO₂Et)₂ Formed by the action of malonic ether on glyoxal in presence of conc ZnCl, Aq (Polonowsky, A 246, 2) Oil, not volatile with steam

Tetra oxy butane tri carboxylic acid CO₂H CH(OH) CH(OH) CH(OH) C(OH)(CO₂H)₂. Formed by oxidation of levulose carboxylic acid by dilute HNO₂ (Dull, B 24, 848) - K₂HA''' Large prisms — Ca₂A'''₂6aq

OXY-BUTANE PHOSPHONIC ACID

C₂H, CH(OH) PO(OH)₂ [168°] Formed from isobutyric aldehyde by successive treatment with PCl, and water (Fossek, M 5, 640) Trimetric crystals, a b c = 97 1 3 94

OXY - ISOBUTANE SULPHONIC ACID CMe₂(OH) CH₂SO₂H Formed from ammonium sulphite solution and isobutylene bromide or CH_Br CMe_OH (Guareschi a Garzino, Ann. chim farm. [4] 6, 110, 9, 96) —BaA'₂ 1½aq -NaA' plates (from alcohol)

m form. [2] 0, ...
plates (from alcohol)
DI-OXY BUTYL-BENZENE O, H₁,O₂ s.s.
CHOH (200°) Formed C.H. CH(OH) C.H. CH.OH (200°) Formed by the action of sodium-amalgam on an alcoholic solution of CaH, CO, CaH, CHO which is got from phenyl propyl ketone by successive treatment with CrO_2Ol_2 and water (Burcker, C.R.94, 220). Syrup. Forms only $C_{10}H_{12}(OAo)_2$ ISOBUTYL o-OXY BENZOIC ACID

C.H.(C.H.)(OH)(OO,H [4 2 1]) Formed from C.H.(C.H.)(ONa and OO, at 140° (Dobrzyck, J pr [2] 36, 391) Needles — CaA', 6aq — BaA', 2aq needles, y sol water Ethers MeA' [54°] (266°) —EtA' (276°) —C₆H₃A' [68°] Formed from the acid, Oil —C₆H₅A'

phenol, and POCl, Converted by long boiling into C₁₇H₁₈O₂ [158°]

DI OXY-BUTYLENE O.H. (OH). Crotonylene glycol (197°) SG 2 1 0616, 22 1 0465 Obtained by the action of boiling baryta on its formyl derivative which is formed when erythrite is distilled with formic acid (Henninger, B 5, 1060, A Ch [6] 7, 215) Liquid, sol water Yields C,H,(OAc), (203°

DI-OXY-DI BUTYL DIKETONE

 $\begin{array}{ccccc} Anhydride & \begin{array}{ccc} \mathrm{CH_2} & \mathrm{CH_2} \\ \mathrm{OHMe} & \mathrm{O} \end{array} > \mathrm{C} < \begin{array}{c} \mathrm{CH_2} \\ \mathrm{O} \end{array} & \begin{array}{$ Formed, together with CO₂, by heating its carb oxylic and CH₂ CH(CO₂H) C CH₂ CH₂ CH₂ CH₂ CH₄ (divalonic acid) [130°] which is got by the action of NaOHAq at '90° on 'divalolactone,' the pro duct of the action of NaOHAq on valerolactone (Fittig, 256, 128) Liquid Volatile with steam

OXY BUTYL MALEIC ACID Lactons Propaconic [124°] Formed by distilling the bromide of propyl itaconic acid with steam, the acid re mains behind and is extracted with ether (Fittig, 4 256, 108) — Needles — BaA'

OXY ISOBUTYL MALONIC ACID C, H12O, te C₄H₂ C(OH)(CO₂H)₂ [110°-114°] Obtained from C,H,CCl(CO,Et), and KOHAq (Conrada Bischoff, B 13, 600, 14, 617, Guthzeit, A 209, 237) Deliquescent mass, v e sol water

DI OXY ISOBUTYL METAPYRAZOLE

O'H' OH -N C(OH) O,H12N2O2 \$ 6 [2100] C(OH) N/

Obtained by boiling with dilute HCl the product (C.H. CH(CN) NH CO NH.) of the action of urea upon valeric aldehyde-cyanhydrin Small white needles M sol alcohol and hot water, sl sol cold water Dissolves readily in alkalis (Pinner a. Lifschutz, B 20, 2356)

OXY BUTYL SUCCINIC ACID The salts are got by the action of bases on the anhydride $Ca(\breve{C_0}H_{12}\breve{O_5})$ 5aq —BaA" 2aq —Ag₂A" Anhy dride OHPr OH(00,H) OH, Propyl para conic acid [78 5°] Formed by heating butyrio aldehyde with sodium succinate and Ac.O (Schmidt, A 255, 68) Needles (from ligroin) Yields heptenoic acid and oxy heptoic lactone on distillation — Ca(C₂H₁₁O₄), 2aq —BaA'₂ —AgA'. Ethyl ether EtA' (c 214° at 96 mm)

Oxv-isobutyl-succinic acid Salts. -

Ba(C₂H₁₂O₃)₂2aq —Ag₂A"
Anhydrids Formed, like the preceding ısomeride, usıng ısobutyrıc aldehyde (Zanner, A. 255, 86) $-Ba(C_0H_{11}O_4)$, $3aq -C_0AA'$, 2aq -AgA'OXY - BUTYRAMIDINE $C_4H_{10}N_2O$ t

CMe.(OH) C(NH) NH. The crystalline hydro-chloride is formed from oxy-butyrimido-ethyl ether and NH, (Pinner, B 17, 2009) It is v. e. sol water

c OXY n BUTYRIC ACID C₁H₂O₃ te CHEt(OH) CO₂H₁ Mol w 104 [43°] Formed by the action o, moist Ag₂O upon bromo-nbutyric acid (Naumann, A 119, 115, Friedel a. Machuca, A 120, 279), and by the action of HCy and HCl on propionic aldehyde (Prschibiteck, B 9, 1312) Formed also by reduction of ethylglyoxylic acid Deliquescent crystals Yields propionic acid on oxidation (Markownikoff, A 176, 309, Ley a Popoff, A 174, 61) —Ca'A, 6aq

ZnA, 2aq S 2 35 at 18°—AgA' prisms

Ethyl ether EtA' (167° 1 V) S G 2

1 004, 12 995 (Schreiner, B 12, 177, A 197, 21). Yields ethyl glyoxylic ether on oxidation (Aristoff a Demjanoff, C C 1887, 1157) Acetyl derivative CHEt(OAc) CO.Et (198°) (Gal, A 142, 373) Butyryl derivative (215°)

Methyl derivative CHEt(OMe) CO.H. Formed from its Me and Et ethers which are made by the action of NaOMe on brome butyric ether (Duvillier, C R 86, 47, 1026, 87, 931, (B), 1020, 87, 981, 88, 598, A Ch [5] 17,528) Liquid, sol water —AgA'—MeA' (150°-155° 1 V)—EtA' (160°) (D), (148° 1 V) (Schreiner, A 197, 16) Ethyl derivative CHEt(OEt) CO₂H.

Formed from its ether, which is made from brome butyric ether and NaOEt Liquid, v sol water —KA' —BaA', —AgA' —MeA' (157°) -

EtA' (168°-174°) (D), (169° 1 V) (S)

Methyl derivative of the a

CHEt(OMe) CONH, [78°] Formed the amide CHEt(OMe) CONH, [78°] CHEt(OMe) CO2Me and alcoholic NH, (D) Slender needles, v sol water

Ethylderiva**tive** of the amide CHEt(OEt)CONH₂ [69°]

B Oxy n butyric acid Laminæ, sol water

CH, CH(OH) CH, CO2H Occurs in urine and blood of diabetic patients (Kulz, Zeit Biol 20, 165, 23, 329, Minkowski, Fr 24, 153, Stadelmann, Zert Biol 32, 456, Wolpe, C C 1887, 277, Hugounenq, Bl [2] 47, 545, Deichmuller, Szymanski, a Tollens, A 228, 92) Formed by reducing acetoacetic acid with sodium amalgam (Wishcenus, A 149, 205), and from propylene chlorhydrin by successive treatment with KCy and KOH (Markownikoff, A 153, 237) Obtained also by oxidising aldol with moist Ag₂O (Wurtz, C R 76, 1165) Thick syrup, volatile with steam Decomposes at 130° into water and (a)-crotonic soid When prepared from urine it is levorotatory, [a]_p = -234 - NaA' very deliquescent needles - ZnA'₂. - CuA' - AgA'

Ethyl derivative CH, CH(OEt) CH, CO, H (c 215°) Formed by the action of HCl on the nitrile, which is formed by combining allyl cyanide with alcohol (Pinner, **B** 12, 2057)

Amide CH, CH(OEt) CH, CONH, [71°] y Oxy n-butyric acid

CH₂(OH) CH₂ CH₂ CO₂H Obtained by the action of boiling lime- or baryta water upon its lactone, which is formed by treating succinyl chloride, dissolved in HOAc and ether, with sodiumamalgam (Saytzeff, B 6, 1255, A 171, 270, J pr [2] 25, 66, Bl [2] 37, 540) Formed also from CH₂Br CH₂CH₂OH by successive treatment with alcoholic KOy and potash (Frühlung, M 8, 700), and by boiling oxy-ethyl-acetoscetic ether with conc baryta-water (Chanlaroff, A. 226, 825) Inquid, which volatilises in the cold Volatile with steam Sol water. Forms the

lactone slowly in the cold, more quickly on heating Chromic acid mixture oxidises it to succinic acid —KA' deliquescent tufts —NaA' -ZnA'₂ (dried at 100°) —BaA'₂ (dried at 110°) dendritic mass (from alcohol)

Lactone CH2 CH2 CO (206°). S G **§ 1 1441**, **§ 1 1286** ĆE (0° to 16°) 00086 Butyrolactone Formed as above Formed also by heating the lactonic acid of γ oxy ethyl malonic acid at 120° (Röder, A 227, 22), and by heating γ chloro butyric acid at 200° (Henry, C R 101, Mobile liquid, miscible with water, but separated therefrom by K2CO2 May be con verted into n-butyric acid by successive treat ment with HI and sodium amalgam

a - Oxy isobutyric acid (CH₂)₂C(OH) CO₂H Acetonic acid Butylactic acid [79°] (212°)

Formation —1 From acetone, HCy, and HClAq (Stadeler, A 111, 320) —2 From bromo isobutyric acid and moist Ag₂O or Na₂CO₂Aq (Markownikoff, A 146, 339, 153, 228, 251, Fittig, A 200, 70) —3 From dimethyl oxalate by treatment with ZnMe, followed by water (Frankland a Duppa, A 133, 80, 135, 25) — 4 By oxidising isobutyric acid with alkaline KMnO, (R Meyer, A 219, 240) -5 By oxidising dı oxy pentane (amylene glycol) with diluted HNO, (Wurtz, A 107, 197)—6 By heating acetone chloroform with water at 180° (Will gerodt, B 15, 2807, Bl [2] 89, 157) Hygro scopio needles, v e sol water, alcohol, and ether Volatile with steam Sublimes at 50° Yields acetone and acetic acid on oxidation Phenyl hydrazine at 160° forms a ψ-phenyl hydrazide [152°] converted by nitrous acid into a nitrosamine [98°] (Reissert a Kayser, B 22,

Salts — BaA', — ZnA', 2aq hexagonal plates, sl sol water S 6 at 15°—AgA' stel hexagonal 8 7 late groups of nacreous scales

Ethyl ether EtA' (151°) Ethyl derivative (CH Ethyl derivative (CH,),C(OEt) CO,H (180°) S G § 1 0211, 16 1 0101 Formed from CMe,Br CO,H and KOEt (Hell a Waldbauer, B 10, 449) —BaA', aq —PbA', aq —ZnA', —AgA' plates m sol water —EtA' (155°)

Isopropylidene derivative C₁₁H₂₀O₄ te CMe₂(O CMe₂ CO₂H)₃ (197°uncor) V D 120 3 (calc 124) Formed by the action of KOH (8 mols) on acetone chloroform (2 mols) and acetone (1 mol), or upon a mixture of chloroform (1 mol) and acetone (2 mols) (Willgerodt, B 20, 2445, Engel, C R. 104, 688) Liquid, converted into oxy isobutyric soid by heating with water — CaA" 1½aq — BaA" ½aq — PbA" (W), PbA" 2aq (E) — ZnA" aq small scales (W), ZnA" 2aq (E).

Nitrile v Acetone Cyanhydrin, vol i.p 31 Anhydride C.H.O. s.s. O(CMe.CO.H.).
Dibutylactic acid A product of the action of alcoholic potash on chloro isobutyric acid (Balbiano, J 1878, 704, 1880, 789) Amorphous, v sol water — Na, A". deliquescent

as-Di-oxy-butyric acid

CH, CH(OH) CH(OH) CO,H [80°]. Formed by boiling bromo-oxy butyrio soid with water (0 Kolbe, J.pr [2] 25, 890), and by heating β -methylglycidic acid with water at 100° in sealed tubes (Melikoff, J. R. 16, 526, B 21, 2055). Mass of slender needles, v e sol water, not volutile with steam.—AgA' needles Gives a silver mirror when boiled with water.

(c 228°) Liquid. Ethyl ether EtA' Anhydrade v. Methyl-glydidic acid βγ-Di-oxy-butyric acid

CH₂(OH) CH(OH) CH₂ CO₂H Butylglyceric acid Formed from CH2(OH) CH(OH) CH2Cl by successive treatment with KOy and dilute HNO, (Hanriot, A Ch [5] 17, 106) Formed also by warming its anhydride with water (Melikoff, B15, 2587) Thick liquid, v sol water, alcohol, and ether -BaA' amorphous

Anhydride CH2 CH CH2 CO2H Butul-

plycidic acid Formed from (3) crotonic acid by successive treatment with HOCl and alcoholic potash Mobile liquid Unites with HCl, forming chloro oxy butyric acid [99°] The ether C₄H₂EtO₃ (145°-150°), S G 21.5 9931 is formed by the action of sodium amalgam on a mixture of epichlorhydrin and chloroformic acid (Kelly, B. 11, 2225)

Di-oxy-1sobutyric acid CH2(OH) CMe(OH) CO2H [100°] Formed from a methyl glycidic acid $(q \ v)$ by warming with water at 100° (Melikoff, $J \ R \ 16, 535$) Prisms, v sol water -KA' aq small prisms

Tri-oxy-isobutyric acid (CH₂(OH))₂C(OH) CO₂H [116°] Formed from glycerose by successive treatment with HCy and HCl (Fischer a Tafel, B 22, 106) Prisms (from alcohol), insol benzene HIAq followed by zinc dust yields isobutyric acid - CaA', 4aq -PbA'2 aq needles, sl sol hot water

A tri-oxy-butyric acid is also formed in the oxidation of gallic acid and tannin by dilute

HNO, (Böttinger, A 257, 248) References - Bromo- and CHLORO-OXYBUTYRIC

ACIDS.

β-OXY-n-BUTYRIC ALDEHYDE v. ALDOL. a OXY-ISOBUTYRIC ALDEHYDE

CMe2(OH) CHO (c 90°) Obtained by boiling with HOAc the compound C12H28O3 formed by the action of NaOC,H, on iodoform (Gorboff, J pr. [2] 41, 248) Mobile liquid, exidised by Ag.O to exy-isobutyric acid [79°] Forms with water a hydrate [c 70°] Polymerises on stand-ing, forming prisms [c 65°] v sol water

Di-isobutyl derivative of oxylsobutyric CMe₂(OC₄H₉) CH(OH)(OC₄H₆) orthaldehyde (125°) 8 G º 9041 One of the products of the action of iodoform (or iodine) on NaOC, H, Oil, with bitter taste Converted by HOAc into isobutyl acetate and oxyisobutyric aldehyde
OXY BUTYRIC IMIDO-ETHYL ETH

ETHER CMe₂(OH) C(NH)OEt The hydrochloride C₂H₁₂NO₂HCl is formed from acctone, HCy, alcohol, and HCl (Pinner, B 17, 2009) crystalline

OXYBUTYROCYAMINE & GUANIDO BUTYRIO

OXY-CAFFEINE v. CAFFEINE

OXY-CAMPHOR v. CAMPHOR and CAMPHOLENIC

OXY-CAMPHORAMIC ACID v. CAMPHORIC

OXY-CAMPHORIC ACID v CAMPHORIC ACID. OXY-CAMPHORIC ANHYDRIDE v. CAM-PHANIC ACID

OXY-CAMPHORONIC ACID & CAMPHORONIC

OXY CAPROIC ACID v OXY-HEXOIC ACID OXYTRICARBALLYLIC (ACID Methyl derevative C.H.(OMe)(CO.H). Formed by heating (C.H.),C(OMe) CO.H with dilute HNO, (Schatzky, J. R. 17, 85) Syrup—CaH.4A'''. jaq—BaH.A'''. 2aq

OXY-CARBOSTYRIL & DI OXY-QUINOLINE OXY-CARBOXYLIC ACID v BENZENE TRI-QUINONE

OXY-0 CARBOXY-PHENYL-ACETIC ACID CO₂H C₆H₄ CH(OH) CO₂H Formed CO2H CH CO CO2H and sodium amalgam Quickly changes, when (Scherks, B 18, 381) set free, to the anhydride (phthalide carboxylic acid) [149 5°]

Oxy-carboxy-d1-phenyl acetic acid C₆H₄(ČO₂H) CPh(OH) CO₂H [c 80°] Formed by warming benzil o carboxylic acid with alkalis (Graebe, B^{21} , 2003) — K_2A'' 2aq

Di-oxy-di-carboxy-phenyl acetic acid TriC₆H(OH)₂(CO₂Et)₂ CH, CO₂Et ethyl-ether [98°] Formed from acetone dicarboxylic ether and sodium (Cornelius a Pechmann, B 19, Needles (from alcohol), insol water

Y-OXY O-CARBOXY-PHENYL-BUTYRIC ACID Lactone C₁₁H₁₀O₄ [121°] Formed by reducing the anhydride of carboxy benzoyl propionic acid with sodium amalgam (Roser, B 17, 2773) $-AgC_{11}H_{5}O_{4} -Ag_{5}C_{11}H_{10}O_{5}$

An isomeric lactone [140°] is obtained by reducing phthalyl propionic acid (Gabriel a Michael, B 11, 1681) — BaC₁₁H₁₀O₅ - BaC₁₁H₂O₅ - AgC₁₁H₂O₄ - AgC₁₁H₂O₄

ACID Lactone C10H8O41e CH_CH, CO,H Formed by reducing \co/

phthalyl acetic acid with sodium amalgam, and acidifying (Gabriel a Michael, B 10, 1558, 2200) Needles (containing aq) AgC10H7O4, Ag2C10H8O5, and BaC10H8O5 2aq

Tri oxy-carboxy-phenyl propionic acid -CH, CO.H **Lactone** $\begin{bmatrix} 4 & 3 & 1 \\ 2 & 2 \end{bmatrix}$ $C_eH_2(OH)$ CO

[228°] Formed by reducing its di methyl de rivative (meconic acetic acid) with HI and P (Liebermann a Kleemann, B 19, 2293) Tables Gives a blue colour with FeCl

Ethyl ether EtA' [c 131°] Crystalline OXYCHRYSOQUINONE v CHRYSOQUINONE Crystalline OXYCINCHENE v CINCHENE

OXYCINCHONIDINE v Cinchonidine

OXY-CINNAMIC ACID v COUMARIC ACID a-Oxy cunnamic acid C₆H₅ CH C(OH) CO₂H Formed in small quantity in the preparation of the isomeric phenyl-glycidic acid by the action of alcoholic potash on C₆H, CHBr CH(OH) CO₂H (Plochl, B 16, 2821) Readily decomposes, yielding phenyl-acetic aldehyde and di oxy-

phenyl propionic scid Phenyl derivative C₆H₅CH C(OPh) CO₂H [180°] Formed by heating sodium phenoxy-acetate with benzoic aldehyde and Ao₂O (Oglialoro, O J. 40, 276)
Prisms —AgA' prisms (from water)
(8, 2, 1)-Di-oxy-cinnamic acid

[8 2 1 CH (OH), OH CH CO2H

Anhydride C.H. (OH) CH CH. m-Oxy-

coumarın [280°-285°] Formed by heating pyrocatechin with realic acid and H.SO. (Bezzarı, G 15, 34) Needles, sl sol cold water Reduces salts of Au, Cu, and Ag

(4, 3 1) Di-oxy-cinnamic acid v CAFFEIC

(5, 2, 1)-D1-oxy cinnamic acid [5 2 1]C,H,(OH),CH CH CO,H

Anhydride [5] C.H. (OH) CH CH

[250°] Formed by heating a mixture of hydroquinone, malic acid, and H2SO4 (Pechmann a Welsh, B 17, 1648) Needles, v sol alcohol Yields an acctyl derivative [147°] crystallising in needles The methyl derivative [103°] is got from [5 2 1] C₆H₃(OMe)(OH)CHO by boiling with Ac O and NaOAc (Tiemann a Muller, 14, 1996)

o Methyl derivative [5 2 1]C₀H₃(OH)(OMe)CH CH CO₂H [180°] Obtained from C6H3(NH2)(OMe)CH CH CO2H by the diazo reaction (Schnell, B 17, 1387) Crystals

Di-methyl derivative C₆H₃(OMe)₂CH CH CO₇H [143°] Obtained by methylating the o methyl derivative Needles Yields di methyl gentisic aldehyde on oxidation with KMnO

(4, 2, 1) Di oxy-cinnamic acid v Umbellic ACID

ap di oxy cinnamic acid Phenyl-methyl C.H. (OMe) CH C(OPh) CO,H derivative [200°] A product of the action of anisic alde hyde and Ac₂O on sodium phenoxy acetate (Valentini, G 14, 147) Rectangular tablets, sol hot alcohol — MeA' [100°] Laminæ

Anhydride of the phenyl derivative

C₁₃H₁₀O₃ [113°] Formed from salicylic alde

hyde, Ac₂O, and sodium phenoxy acetate (Oglia loro, C C 1887, 1164) Yellow prisms, v sl sol hot water

Tri oxy cinnamic acid v ÆSCULETIC ACID and DAPHNETIN

Tetra-oxy cinnamic acıd Dr methyl methylene ether

 $C_6H(O_2CH_2)(OMe)$, CH CH CO_2H [196°] Formed from apiolic aldehyde, Ac₂O, and NaOAc (Cia mician a Silber, B 22, 2485) Small yellow needles (from hot alcohol), sl sol ether and hot water

OXY-CINNAMIC ALDEHYDE v COUMARIC ALDEHYDE

Di-oxy cinnamicaldehyde Methyl derevative v FERULIC ALDEHYDE **OXY-CINNOLINE**

 $C_sH_oN_2O$ se $C_oH_4 < \stackrel{C(OH)}{N} \stackrel{CH}{== N}$ [225°] Formed by heating its carboxylic acid at 260° (Richter, B 16, 681) Small prisms, v sol alcohol and ether, sl sol water May be sublimed Sol Na₂CO₃Aq —B'₂H₂PtCl₄ small prisms

Oxy-cinnoline carboxylic acid $C_eH_4 < N - N - N$ [c 265°] Formed from

o diazo phenyl propiolic acid by heating with water at 70° Colourless needles or scales, sol HClAq, sl sol alcohol, nearly insol water OXY-CITEACONIC ACID C₅H₅O₅ 2 c.

 $0 <_{\mathrm{CH}}^{\mathrm{CMe}} \, {}_{\mathrm{CO_{2}H}}^{\mathrm{CO_{2}H}}$ [162°] Formed from citracontc acid by successive treatment with HOCl and alkalıs (Morawski, J pr [2] 10, 69, 11,

430, Scherko, A 227, 233, Michael, J pr [2] 40, 171, Melikoff a Feldmann, A 253, 89). Prisms (containing aq) Hot water converts it into propionic aldehyde and CO. With HBr is forms C,H,BrO, [156°] HCl yields, in like manner, CO,H CClMe CH(OH) CO,H [162°]

Salts - (NH,),A" - (NH,)HA' - KHA" -

BaA" 4aq — SrA" 4aq — PbA" 4aq Ethyl ether Et₂A' (255⁵) S G ² 11376; ²² 11167 CE (0°-22°) 0008507

OXY-CITRIC ACID C.H.O. 16

Occurs in beetroot (Lipp- $C_3H_3(OH)_2(CO_2H)_3$ mann, B 16, 1078) Formed from aconitic acid by successive treatment with HOCl and limewater (Pawolleck, A 178, 150) Deliquescent mass, v e sol water —Salts Ba,A", 5aq - $Ca_3A'''_29aq$ — $Ca_3A'''_210aq$ — $Cd_4(C_6H_4O_8)_26aq$ — $Cu_4(C_6H_4O_8)_2xaq$ — Et_2A''' oil with bitter taste.

OXYCOBALTAMINES v vol 11 p 224

OXYCOMENIC ACID v COMENIC ACID

OXY CONICEINE v Contine

OXY-COPAIVIC ACID v COPAIVIC ACID

OXY COUMARIC ACID v DI OXY CINNAMIO ACTD

OXY-COUMARILIC ACID v COUMARILIC

OXY-COUMARIN v Anhydride of Di-oxy-CINNAMIC ACID and UMBELLIFERONE

Di-oxy coumarin v Daphnetin OXY COUMARONE v COUMARONE

β OXY CROTONIC ACID Methyl deriva-tive CH, C(OMe) CH CO₂H [128 5°] Formed from 8 chloro crotonic acid and NaOMe (Fried rich, A 219, 327, 334) Crystals, insol water

Ethyl derivative CH, C(OEt) CH CO.H [137 5°] Formed from CH₃ CCl CH CO₂Et and alcoholic potash Prisms, v sol alcohol and ether -KA' plates -KA' 3aq needles -EtA' [30°] Decomposed by dilute H₂SO₄ into acetone, CO₂, and alcohol

Phenylderivative CH, C(OPh) CH CO2H [150°] Formed by heating sodium & chlorocrotonate or & chloro isocrotonate with NaOPh (Autenrieth, A 254, 240) Crystals, v sl sol hot water Yields CH₃ C(OPh) CH₂ (162°) on heating

The above compounds may be viewed as deri

vatives of acetoacetic acid (q v)

a Ovv-isocrotonic acid This acid is not known in free state, for, like the preceding isomeride, it would at once change to acetoacetic acid

Methyl ether of the methyl derivative CH, C(OMe) CH₂ CO₂Me (175°) S G 15 10235 Formed from CH₂ CCl CH₂ CO₂Me and NaOMe (Enke, A 256, 205)

Methyl ether of the ethyl derivative CH₂ C(OEt) CH₂ CO₂Me [12°] (195°) S G 15 999

Ethyl ether of the ethyl derivative (195° cor) CH, C(OEt) CH2.CO,Et [29°] Formed from β chloro isocrotonic ether and

NaOEt (Koll, A 249, 324) Plates
Propyl derivative of the methyl ether
CH₂ C(OPr) CH₂ CO₂Me (230°) S G 961

Isobutyl derivative of the methyl ether CH, C(OC,H,) CH, CO,Me (253°). S G

a-Oxy-isocrotonic acid CH, CH CH(OH) CN Formed from acrolein, KCy, and HOAc (Lobry de Bruyn, R T. C 4,

Isomerides v Oxy METHACRYLIC ACID and ACETOACETIC ACID

OXYCUMENE v CUMENOL

Di-methyl derivative D1-oxy cumene C.H.C.H.(OMe)2. (246°) Formed by the action of sodium on an alcoholic solution of CeH3(C3H3)(OMe)2 (268°), which is got by boiling the isomeric methyl ether of eugenol with alcoholic potash (Ciamician a Silber, B. 23, 1164) Colourless oil

m-D_{1-ω} oxy ψ-cumene $C_6H_3(CH_3)(CH_2 OH)_2[4 3 1]$ [77°] Formed by boiling m di ω bromo ψ cumene with aqueous V sol water and alcohol, al sol ether (Hjelt a Gadd, B 19, 867)

Isomeride v Hydro-\psi-cumoquinone

Tri oxy-cumene. Di-methyl derivative $C_6H_2(C_3H_7)(OMe)_2(OH)$ (278°) Formed by reduction of iso-apiol (Ciamician a Silber, B Thick liquid, sol KOHAq. 23, 2285)

Isomeride v PROPYL PYROGALLOL

OXY-CUMIDINE v Amido cumenol.

OXY n-CUMINIC ACID

 $\begin{array}{lll} \textbf{C}_{\bullet}\textbf{H}_{\bullet}\textbf{Pr}(\textbf{OH}) & \textbf{CO}_{2}\textbf{H} & \textbf{S} & \textbf{2} & \textbf{1} \\ \textbf{0}-\textbf{propyl} & \textbf{phenol}, & \textbf{Na, and } & \textbf{CO}_{2} & \textbf{Spica, } & \textbf{J} & \textbf{1878,} \\ \textbf{585} & \textbf{--BaA'}_{2} & \textbf{2}_{3}\textbf{aq} & \textbf{--PbA'}_{2} & \textbf{2}_{3}\textbf{aq} & \textbf{-AgA'} & \textbf{pp} \\ \end{array}$

Oxy n cuminic acid

C₆H₃Pr(OH) CO₂H[5 2 1] [98°] Formed from p-propyl phenol, Na, and CO₂ (Spica) Coloured violet by FeCl₁ —BaA'₂ 3aq — PbA'₂ 2aq —AgA'

Oxy-cuminic acid C.H.Pr(OH) CO₂H [4 2 1] [98°] Formation —1 By fusing carvacrol with potash (Jacobsen, B 11, 1063) -2 By fusing isocymene sulphonic acid with potash (Jacobsen, B 12, 432) -3 From amido cuminic acid by the diazo-reaction (Widman, B 19, 270)

Properties —Flat needles or leaflets

verted by HCl at 190° into m propyl phenol [26°]

(228° 1 V) FeCl, gives a reddish violet colour. Yields CaA', and BaA', Oxy cuminic acid C.H.Pr(OH)CO.H[4 3 1] [141°] Formation—1 From amido cuminic acid (Cahours, A Ch [8] 53, 338, Lippmann a Lange, B 13, 1662)—2 Among the products got from thymol by potash fusion (Barth, B 11, 1571)—3 By oxidation of potassium cumylsulphate C.H.MePr O SO.K [1 4 3] or cumylphosphate C₆H₃MePr O.PO₃K₂[1 4 3] with alka line KMnO, and saponification of the resulting sulphate or phosphate (Heymann a Königs, B 19, 3306)

Properties —Slender needles, sl sol cold water Not attacked by conc HClAq at 200°

Salts — NaA' 2aq — Na $_2$ C $_{10}$ H $_{10}$ O $_3$ 1 $_2$ aq — BaA' $_2$ aq — CdA' $_2$ aq — AgA' white pp

Ethyl ether EtA' [75°] Prisms Ethyl derivative C.H.Fr(OEt) CO.H. [140°] Crystalline powder —CdA'_2—AgA'
Oxy o cuminic acid C.H.Fr(OH) CO.H [3 2 1]

[72°] Formed, together with C.H. Pr(OH)(CO.H)₂ [295°], from isopropyl-phenol, Na, and CO₂ (Fileti, G 16, 126) Colourless needles FeCl. colours it violet

Oxy-o-cuminic acid C.H.Pr(OH)CO.H [5 2 1]. [121°] Obtained from p-isopropyl-phenol, sodium, and CO₂ (Paterno, J 1878, 806) Formed also by fusing m-isocymenol with KOH (Jesurun, B 19, Flat needles FeCl, colours its solution 1415) deep bluish-violet.—CaA'..—BaA'.—AgA.

An isomeride [166°-170°] is got by fusing 8isocymene sulphonic acid with potash (Jacobsen, B 12, 433)

Oxy ψ-cuminic soid C_cHMe_s(OH)CO₂H [6 5 8 2 1] [181°] Formed from sodium ψ cumenol and CO_2 (Krohn, B 21, Needles, v sol ether

Oxy-ψ-cuminic acid

 $C_6HMe_3(OH)CO_2H[1 3 4 5 6]$ [148°] Formed by fusing durenol with potash (Jacobsen a Schnapauff, B 18, 2844) Small needles, nearly ınsol cold water HClAq at 200° yıelds ψ cu menol [93°] —CaA', 2aq prisms, sl sol cold Aq

Dı oxy y cuminic acıd $\rm C_6Me_3(OH)_2CO_3H\,[6~4~3~5~2~1]$ [210°] Formed by reducing ψ cumoquinone carboxylic acid with zinc dust and aqueous NaOH (Nef, B 18, 3498, A 237, 13, $C \bar{J}$ 53, 428) Needles, m sol hot water Reduces ammoniacal AgNO₃. Its alka

line solution turns violet in air Ethylether EtA' [109°] Needles

OXY-V CUMINIC ALDEHYDE C10H12O2 1 e C₆HMe₈(OH)CHO [6 5 3 2 1] [106°] A product of the action of chloroform and NaOHAq upon

ψ cumenol (Auwers, B 17, 2976) Needles

DI-0XY DI ψ CUMYL C₁₈H₂₂O₂ ι ε

C₆HMe₅(OH) C₆HMe₅(OH) [173°] Formed in $C_eHMe_s(OH) C_eHMe_s(OH)$ the preparation of ψ cumenol from ψ cumidine by the diazo reaction, and also by oxidation of ψ -cumenol with dilute HNO, (Auwers, B 17, 2982, 18, 2659) Crystals Yields adı bromo derivative [187°] and a di methyl derivative [126°]

α OXY CUMYL-ACETIC ACID C₁₁H₁₄O₂ * e C₂H₄Pr CH(OH) CO₂H [158°] Formed from cuminic aldehyde, HCy, and HCl (Raab, B 8,

1148) Needles -- BaA', 4aq -- PbA',

Oxy di cumyl acetic acid

(C,H, C,H,),C(OH) CO,H [120°] Formed from C,H, C,H, CO CO C,H,C,H, by potash-fusion (Boesler, B 14, 326) Needles $-BaA'_{.2}$ OX.CUMYL-AGRYLIC ACID C₁₂H₁,O₃ $z \in C_0H_1(C,H_1)$ (OH) CH CH CO,H The (4,2,1) acid [176°] and the (4,3,1) isomeride [206°] are formed by the degree rectant from the carry formed by the diazo reaction from the corre sponding amido- acids Both are crystalline (Widman, B 19, 268, 417)

DI OXY DI CUMYL PYRAZINE DICARB OXYLIC ACID

[143] CO.H.O.H.Pr NCCHOHOCOH) NO.H.Pr.CO.H Formed by boiling CH2Cl CO NH C6H3Pr CO Me with alcoholic potash (Abenius, J pr [2] 40, 440) Insoluble powder —Et.A" [193°]

OXYCYANCONIINE v CYANCONIINE

OXYCYANETHINE v CYANETHINE

OXY CYCLOPIN C₁₅H₂₀O₁₆ A glucoside in

Cape Tea split up by dilute acids into oxy
cyclopic acid C₁₆H₂₂O₁₂ and glucose (Greenish, Ph [3] 11, 569)

DI-OXY DIOYMYI C₂₂H₂₂O₂ t c C₄H₂Me(O₂H₂)(OH) C₄H₂Me(O₂H₂)(OH) [165 5°] Formed by oxidising thymol with iron alum (Dianin, J R 14, 185) Prisms or tables (con

taining aq), v sol alcohol

OXY CYMYL-ACRYLIC ACID C₁₅H₁₀O₃ * 6 [2 5 6 1] C₄H₂Me(C₂H₂)(OH) CH CH CO₂H The anhydride [53°] (220°-280°) is formed by heating thymol with malic soid and H₂SO₄ (Pechmann a. Welsh, B 17, 1647)

The isomeric (2,5,4,1)-acid 280°] is formed from thymotic aldehyde, NaOAc, and Ac₂O

(Kotek, B 16, 2104) It yields a crystalline

methyl derivative [141°]

DI OXY-DI CYMYL-ETHANE C22H30O, 1.6. OH, CH(C₁₀H₁₂ OH)₂ [185°] Formed from thymol, paraldehyde, chloroform, and SnCl₄ (Steiner, B 11, 287) Needles (from benzene). Yields C₂₂H₂₈(OEt), and C₂₂H₂₈(OAc), [100°] DI OXY-DI-CYMYL ETHYLENE

CH₂ C(C₁₀H₁₂OH)₂ [171°] Formed, together with the preceding body, from CCl₂ CH(C₀H₁₂OH)₂ by boiling with alcohol and zinc-dust (Jaeger, B 7, 1198, C J 31, 263) Oxidised by alkaline K.FeCy, to C.,H.,O. [215°] and C.,H.,o. [215°]. DI OXY DI CYMYL SULPHIDE

 $(C_0H.MePr(OH))_0S$ [153°] (Tassinari, G 17, 83) DI OXY DECANE $C_{10}H_{22}O_2$ Decylene glycol Dramylene glycol The diacetyl derivative, formed from di bromo decane and AgOAc, yields on

saponification with KOH the anhydride CieH20 (diamylene oxide) (Bauer, J 1862, 450)

D1 - oxy - decane CMePr(OH) CMePr(OH) Methyl propyl pinacone (c 223°) Formed from methyl n propyl ketone, water, and Na (Friedel, J 1869, 513) Dilute H_2SO_4 converts it into the pinacolin $C_{10}H_{20}O$ (185° uncor) (Szymanski, B 19, 1532) The isomeric $CEt_2(OH)$ $CEt_2(OH)$ $[28^\circ]$ is formed in like manner from di ethyl-ketone (Schramm, B 16, 1584

Tetra oxy-decane Anhydride

CMe(OH) CH₂ CMe
O (270°) Formed from (CH₃ CO)₂CH₂ and sodium amalgam in presence of a dilute acid (Combes, A Ch [6] 12, 230) Liquid, v sl sol water YOXY DECOIC ACID Lactone C10H18O21e

 C_0H_{13} $CH < CH_2 CH_2 CO_2$ (281° uncor) Formed from bromo decoic acid and Na₂CO₂ (Schnee gans, A 227, 92) Yields $Ba(C_{10}H_{19}O_{2})_{2}$ aq and AgC₁₀H₁₉O₈

Oxy decoic acid CH2Pr CH(OH) CHPr CO2H Formed from isovaleric ether and Na (Wohlbruck, B 20, 2332) Needles, v sol hot water -BaA', -AgA' AgOH amorphous.

Oxy decoic acid C₁₀H₂₀O₃ t & C₄H₂ CH(OH) CH(C₂H₇) CO₂H [120°] Formed by the action of alcoholic potash at 110° on C₄H₅ CH(OEt) CH(C₅H₇) CO₂Et, which constitutes half the product of the action of sodium on isovaleric ether (Hantzsch, A 249, 64)

DI OXY-DECYLENE Di-valeryl - deri-O.H.C(O COC,H.) C(O COC,H.)C.H. vative (155°-165° at 12 mm) (Klinger a. Schmitz, B

24, 1275)

DI-OXY-DODECANE CEtPr(OH) CEtPr(OH) (255°) Formed from ethyl propyl ketone, water, and Na (Oechsner de Coninck, Bl [2] 25, 10) Liquid The isomeric 'methyl butyl pinacones' CHMeEt CMe(OH) CMe(OH) CHMeEt (249°) and CMe, CMe(OH) CMe(OH) CMe, [69°] are prepared in like manner (Wishcenus, A 219, 810, Friedel Silva, J 1878, 340)

TRI - OXY - DODECINOIC ANHYDRIDE C₁₂H₁₅O₃ s.s. CH₂ CH₂ CH₂ CCC_{CO} O. D₄hexolactone (above 800°) Formed from oxyhexoic lactone and NaOEt (Fittig, A 256, 185). Liquid, sl sol water

DI-OXY-DODECINENE C12H20. C.H.CH, CMe(OH) CMe(OH) CH,O.H.. (266°).

SG 9 963 CE (0°-24°) 00082 from allyl acetone (Kablukoff, J R 1887, 518)

OXY-DODECOIC ACID $(\underline{C}_3H_{11})_2C(OH)$ CO_2H Diamoxalic acid [122°] Formed from oxalic ether, isoamyl iodide, and zinc (Frankland a Duppa, A 142, 8) Yields EtA' (262°) and Duppa, A 142, 8) C_sH₁₁A' (280°-290°)

OXY - DURYL - ACETIC ACID [6 4 3 2 1] C₆HMe₄ CH(OH) CO₂H [156°] Formed from tetra methyl-phenyl glyoxylic acid, alcohol, and sodium-amalgam (Claus a Foecking, B 20, 3100, J pr [2] 38, 232) Prisms — NaA'1½aq — CaA',28aq — BaA',28aq v sol water The isomeric (5, 4, 8, 2, 1) acid [160° uncor] yields KA'4aq, BaA', 3aq, and CaA', 21aq

 $C_0H_{20}O_2$ DI - OXY - ENNANE Pr CH(OH) CH(OH) CH2Pr [80°] Formed by the action of alcoholic potash on a mixture of isobutyric aldehyde and valeric alde hyde (Fossek, M 5, 120, Swoboda, M 11, 384) Prisms (from water) On boiling with dilute H₂SO₄ it yields a pinacolin C₁₆H₄₆O₂ (274°) Cold cone H₂SO₄ forms C₆H₁₈O (150°)

Di acetyl derivative C12H22O4 (242°) OXY-ENNENOIC ACID C. H18O3 Oxy vinylsso heptoic acid Found among the products got by passing CO over NaOAc mixed with sodic iso amylate at 180° (Poetsch, A 218,78) Thick honey yellow oil, not volatile with steam C₂H₁₄Na₂O₃8aq

Methyl ether C.H. MeO. (c 250°)

OXY-ENNOIC ACID CPr2(OH) CH, CO2H. Formed by oxidising CPr₂(OH) C₃H₃ with KMnO₄ (Schirokoff, J pr [2] 23, 197) Syrup, KMnO₄ (Schirokoff, J pr [2] 23, 197) Syrup sl sol hot water —CaA'₂aq —BaA'₂aq S (o BaA'₂) 9 3 at 20°—PbA'₂ S 16 at 195° prisms AgA'

Oxy ennoic acid Pr CH2 CH2 CEt(OH) CO2H

Crystalline —BaA', —AgA' Ethyl ether EtA' (225°) SG 13 940 A product of the action of isoamyl iodide and zine on oxalic ether (Frankland a Duppa, A 142, 6, Beilstein, Bn 1, 529)

OXY ERUCIC ACID C₂₂H₁₂O₄ Formed from di bromo behenic acid C₂₂H₄₂Br₂O₂ and moist Ag₂O (Haussknecht, A 143, 51) Oil, forming amorphous salts

OXY ETHANE PHOSPHONIC ACID

 $C_2H_1PO_4$ is $CH_1CH(OH) PO(OH)_2$ [76°] Formed from aldehyde (4 mols) and PCl_3 (1 mol), followed by cold water (Fossek, M 7, 32) tals decomposing at 120° —CaA"

OXY ETHANE SULPHONIC ACID v. Is-

ETHIONIC ACID.

Oxy ethane disulphonic acid C₂H₃(OH)(SO₃H). Formed, together with ethane tri-sulphonic acid, by boiling tri-bromo ethane with a saturated solution of ammonium sulphite (Monari, B 19, 1347) — Na₂A"3½aq — (NH₄)₂A"½aq —BaA"2aq very soluble powder Oxy-ethane disulphonic acid

SO,H CH, CH(OH) SO,H Formed from 18 ethionic soid and H2SO, at 100° (Meves, A 143, 196, Engelhardt a. Latschmoff, Z 1868, 271) A" aq needles, v e sol water

OXY - ETHENYL - AMIDO - PHENYL - MER-CAPTAN C.H., NSO . C.H. $\langle S \rangle$ CCH.OH Prepared by heating chloro-acetic acid with amido-phenyl-mercaptan (Hofmann, B 13, 1284) Long fine needles

alcohol and caustic alkalis

DI-OXY-ETHENYL-o-PHENYLENE AMINE C.H.N.O. [above 280°] Obtained by reduction of o-nitro oxanilic acid with SnCl. (Aschan, B. 18, 2939) Sublimes in plates Sol acetic acid, sl sol water, alcohol, and ether, insol benzene, ligroin, and chloroform It has weak acid properties, forming unstable salts—BaA'₂2aq white crystalline pp OXY-ETHYL-ACETOACETIC ETHER

CH₃CO CH(CO₂H) CH₂.CH₂OEt Formed from acetoacetic ether, NaOEt, and glycol chlorhydrin (Chanlaroff, A 226, 326) Liquid, yielding γ oxy butyric acid on boiling with baryta and alcohol

Oxy-d1-ethyl-acetoacetic ether Methyl derivative CH2(OMe) CO CEt2.CO2Et (c 188°) Formed, together with an oil $C_7\hat{H}_{14}O_2$ (c 131°) by the action of NaOMe on chloro di ethylacetoacetic ether (James, A 231, 240)

D1-oxy-d1-ethyl-acetoacetic ether methyl derivative CH(OMe), CO CEt, CO,Et (c 195°) Formed together with the compound CH(OMe), CO CHEt, (134°), by the action of NaOMe on CHCl, CO CEt, CO,Et

OXY-ETHYL DI ALLYL-AMINE

(C,H,),NCH, CH,OH (197°) Formed from di allyl-amme and CH,Cl CH,OH (Ladenburg, B 14, 1879) Liquid base

OXY-ETHYL-p AMIDO-BENZOIC ACID CHOH CH, NH CH, CO2H [187°] Formed from p amido-benzoic acid and ethylene oxide (Ladenburg, B 6, 129) Prisms, sl sol cold water -HA'HNO, crystals

OXY ETHYL o AMIDO PHENOL

CH₂(OH) CH₂ NH C₆H₄OH (290°-310°) Formed from o amido phenol and glycol chlorhydrin (Knorr, B 22, 2095) Liquid, sol water Successive treatment with fuming HCl and NaOHAq forms the anhydride $C_cH_4 < OCH_2 (268^\circ)$

Methyl derivative CH₂(OH) CH₂ NH C₆H₄OMe (305°1 ♥) Formed

from o anisidine OXY - ETHYL - AMIDO - QUINOLINE DI-HYDRIDE v Hydrazido phenyl-propionic acid

OXY-ETHYL-AMINE CH₂(OH) CH₂NH₂ Amido ethyl alcohol Formed by the action of ammonia on ethylene oxide or on glycol chlor-hydrin (Wurtz, C R 49,898, 53,338) Formed also by the action of conc H₂SO₄ on bromo-ethyl phthalimide, by the action of HNO₃ on vinylamine, and by the action of AgNO₃ (2 mols) on bromo ethylamine hydrobromide (1 mol) (Gabriel, B 21, 569, 2666)

Salts -B'HCl [below 100°] -B',H,PtCl B'HBr hygroscopic crystals —B'HNO_s [55°] $-\mathbf{B}'\mathbf{C}_{\bullet}\mathbf{H}_{2}(\mathbf{NO}_{2})_{\bullet}\mathbf{OH}$ [159°] Yellow needles

(from alcohol)

of the acetyl derivative Picrate CH,(OH) CH, NHAcC,H2(NO2),OH. [169°]. (Gabriel, B 22, 2222)

Bensoyl derivative CH2(OH) CH2NHBz [143°] -B'2H2PtCl. -Picrate. -B'HBr

Crystalline pp 195°T

Insol water, sol.

| Benzoyl derivative [98°] (Schreiber, B 24, 189).
| B'HCl [215°] -B'C,H₂(NO₂),0H -Platino| B'HCl [215°] -B'C,H₂(NO₂),0H -Plati

Oxy-tri-ethyl-amine C.H. NO ie NEt, CH, CH, OH (161°) Formed from NEt, H and glycol chlorhydrin (Ladenburg, B 14, 1878, 15, 1144) Liquid, miscible with water

Cinnamoyl derivative NEt₂ CH₂·CH₂OCOC₈H₇ Formed from the cin namate of the base and dilute HCl Yields

B'HAuCl₄ and B'C₆H₂(NO₂)₈OH NEt, Cl CH, CH, OH Ethylo-chloride Prisms (Wurtz, A Suppl 7, 88) -Gold salt

C.H. NOAuCl, golden plates
Di-oxy-ethyl amine Di-ethyl deriva-CH₂(NH₂) CH(OEt) Amido acetal tive (162°) Formed from chloro acetal and alcoholic NH, (Wohl, B 21, 616, Wolff, B 21, 1482) Colourless liquid, v e sol water—B'₂H PtCl_e hexagonal plates, sl sol cold alcohol

Di-oxy-di-ethyl-amine NH(CH2 CH2OH); Formed from ethylene oxide or ClCH₂ CH₂OH and ammonia (Wurtz) —B'₂H₂PtCl₆ tables
Tri-oxy tri ethyl amine N(CH₂CH₂OH)₃ A

product of the action of ethylene oxide on ammonia (Wurtz) With glycol chlorhydrin it yields N(OH)(CH, CH,OH), Both are syrupy

Tetra oxy di-ethyl amine Tetra ethyl derivative NH(CH,CH(OEt)₂)₂ (260°) S 14 Formed from chloro acetal and NH,Aq at 130°

(Wolff, B 21, 1484) —B',H_PtCl_a [121°]

a-OXY-ETHYL AMINE awy-TRI SUL
PHONIC ACID C₃H₂NS₂O₁₀ re

CH₁ C(HO)(SO₃H) CH(SO₃H) NH(SO₃H)

The sodium salt Na,A" 3aq is formed by shaking nitroso acetone CH₃ CO CH(NOH) with a 30 p c solution of sodium bisulphite, and crystallises out on standing as a crystalline powder consisting of white needles It is v sol water, insol alcohol By warming with dilute acids it is split up into methyl-glyoxal (pyruvic aldehyde) CH, CO CHO. sodium sulphate, NH, and SO2 (Pechmann, B 20, **2**543)

OXY-ETHYL-ANILINE NHPh CH2 CH2OH (286°) SG 21110 Formed from aniline and ethylene oxide (Demole, B 6, 1024, Ladenburg, B 6, 131, Knorr, B 22, 2092) Liquid, with strong reducing properties -B'2H,PtCl₆ dish brown crystals

 ω Oxy-di-ethyl-aniline C,H,NEtC,H,OH (268°) Formed from ethyl aniline and ethylene chlorhydrin at 100° (Laun, B 17, 677)

Di-oxy-di-ethyl-aniline NPh(CH₂ CH₂OH)₂. (above 350°) Formed from the preceding and glycol chlorhydrin Treatment with HClAq at 170°, followed by cold caustic soda solution, yields NPh $\langle C_2H_4\rangle$ O [58°] (270°). The compound

 $NPh < 0.H_{\circ}^{\circ} > 0.$ [67°] is formed by the action of alcoholic AgNO, on the corresponding sulphur compound (Holzmann, B 20, 1640)

OXY-ETHYL-BENZENE v ETHYL PHENOL Phenyl derivative CH_(OPh) CH_NH_, (229°). Formed from phenyl oxyethyl phthal-amic acid and cone HClAq (Schmidt, B 22, 1256). Yields an acetyl derivative [78°] and a K_CO, (Zincke, A. 216, 293). Needles (from benzene ligroin) Converted by boiling dilute H.80, into oily C.H.O (260° at 50 mm)

Di-acetyl derivative C.H.Ac.O. (274°

Dr henzoyl derivative [97°] Needles Dr oxy-ethyl benzene C₂H₃Et(OH)₂[134] (29.5°) Formed from p ethyl phenol sulphonic acid by potash fusion (Sempotowski, B 22, 2667) Coloured green by FeCl,

D1-oxy-tri ethyl-benzene C.HEt,(OH)2. Formed by the action of HCl on CeHEts(OEt)(OH) (165° uncor at 20 mm) which is a product of the action of alcoholic potash and EtI on resorein (Herzig a Zeisel, M 11, 306) White needles (from dilute alcohol) Yields C₆HEt₃(OEt)(OAc) [65°] crystallising in monoclinic prisms

OXY-ETHYL BENZOIC ACID C,H₁₀O₂ 4.6
C₆H₁E(OH) CO₂H [120°] Formed from sodium
o-ethyl phenol and CO₂ (Beilstein a Kuhlberg,
4 156, 213) Coloured violet by FeCl,
Oxy-ethyl benzoic acid [112°] Formed in

like manner from sodium phlorol (Oliveri, G 13, 267) Needles (from water) —BaA'₂aq scales \$\beta\$ 0xy ethyl benzoic acid

CH, CH(OH) $C_0H_1CO_2H_2$ — AgA' needles Anhydride $C_0H_3O_2$ (276°) V D 74 (obs) Formed by reducing acetophenone carboxylic acid with sodium amalgam and acidifying (Gabriel a Michael, B 10, 2205) Crystalline

Tri oxy-ethyl-benzoic acid Methylene derivative CH2 CO CoH2 (CH2 CH2OH) CO2H

'a Oxyethylpiperonylcarboxylic acid' [146°] Formed from the corresponding amido- acid CH₂O C₂H₂(C₂H₂NH) CO₂H (Perkin, jun, C J 57, 1021) Crystals Converted at 120°-130° into the anhydride C10H8O4 [127°] -AgC10H9O8 -KA'-NH₃MeA' crystals

TRI OXY TRI-ETHYL BORATE

B(OC,H,OH), [162°] Formed from BCl, and glycol (Councler, J pr [2] 18, 392) Deliquescent crystals

DI OXY ETHYL-BUTYL GLYOXALINE

 $C_{\downarrow}H_{\downarrow}CH < CO NEt_{NH CO}$ [135°] (295°) Formed from isobutyl hydantoin, KOH, and EtBr (Pinner, B 22, 685) Silky needles

OXY-ETHYL CARBAMIC ACID An. hydrids CH2NH>CO [91°] Formed from B bromo ethyl-amine and Ag₂CO₃ (Gabriel, B Flat crystals (from alcohol), v sol water

OXY-ETHYL CONIINE v CONIINE

DI-OXY ETHYLENE DIQUINOLINE OCTO-HYDRIDE C20H24N3O2 2 0

OH CH — COH, CH, OH, OH, OH, OH, OH, C — CH CH OH COH, OH [233°] Formed by heating oxy-quinoline tetrahydride with ethylene bromide (Kohn, C J 49, Small silky prisms 509)

DI-OXY-ETHYLIDENE-DI-NAPHTHOQUIN-

 $C_{\bullet}H_{\bullet} < CO C(OH) C(OH) CO > C_{\bullet}H_{\bullet}$ ONE

Phenyl hydraside

{C₁₀H₄(OH)O(N₂HPh)}₂CHMe [258°] Got by heating the phenyl hydrazide of oxy (a) naphthoquinone with alcohol and aldehyde at 100°

(Zincke a Thielen, B 21, 2205) Small red needles, v sl sol alcohol

TETRA OXY.TETRA ETHYLIDENE. PHOS. PHONIUM CHLORIDE (CH, C(OH)), PCl [112°] Formed from aldehyde, PH, and HCl (Messenger a Engels, B 21, 328) Dimetric crystals, with unpleasant smell, v sol alcohol, insol. ether Decomposed by water The corresponding (CH₂ C(OH)), PBr [88°] is also crystalline The iodide (CH₃ C(OH)), PI [65°] is formed from aldehyde and phosphonium iodide (Girard. $A \ Ch \ [6] \ 2, 11$

DI-OXY-ETHYLIDENE-METAPYRAZOLE

Formed by heating chloro-crotonyl-urea, CH₃ CH CCl CO NH CO NH₂, to its meltingpoint, HCl being evolved Needles M sol. hot water (Pinner a Lifschutz, B 20, 2350)

a OXY-ETHYL MALONIC ACID CEt(OH)(CO,H)₂ Ethyltartronic acid [98°] Prepared by saponification of chloro-ethyl malonic ether with baryta water (Conrad, B 14, 618) Decomposes at 180° into a-oxy-butyric acid and CO2

β Oxy-ethyl malonic acid

CH, CH(OH) CH(CO,H) Formed from ethylidene malonic acid and baryta water (Komnenos, A 218, 163) Syrup —Ag,A" amorphous

γ Oxy ethyl malonic acid CH₂(OH) CH₂ CH(CO₂H)₂ — BaA" 1¹₂aq Got by boiling the lactonic acid with baryta — Ag₂A"

Lactonic acid

Formed by boiling brome ethyl malonic acid with water (Röder, A 227, 19) Obtained also by boiling vinaconic acid with diluted H.SO. -BaA'

A'₂ DI-OXY DI-ETHYL OXIDE

*O(CH(OH) CH₃)₂ Alkoyl derivatives of this body are formed by the action of sodium salts on di chloro di ethylether (Geuther, A 226, 223, 245, 101)

Formyl derivative (c. 180°) 1 134

Acetyl derivative O(CH(192°) SG 18 1 071, 29 1 067 O(CH(OAc) CH3)2 Colourless liquid, slowly decomposed by water into aldehyde and acetic acid

Propionyl derivative (c 218°) 1 027

S G 25

Butyryl derivative (c 238°) S G 22 994

Benzoyl derivative C₁₈H₁₈O₅ Needles Succinyl derivative O(CMeH)₂C₁H₄O₄ Needles

Di-methyl ether O(CH(OMe) CH₃).

7°) SG 155 953 Formed from and di-Formed from aa dichloro-di-ethyl oxide, MeOH, and NaOMe Oil decomposing on standing into di methyl acetal and aldehyde

Di-sthyl sther (153° cor) SG 14 891, Di-propyl ether (184° cor) SG 14 895 Di-isobutyl ether (175° cor) SG 11 875 Di-isoamyl ether (227°) SG 11 874 DI-OXY-DI-ETHYL-DIPHENYL Di-sthyl ether [8 4 1]C.H.Et(OEt) C.H.Et(OEt)[1 8 4]

[120° cor]. Formed from di amido di-ethyl-diphenyl, alcohol, and nitrous acid (Schultz, B 17, 475) White plates, sl sol cold alcohol

Tetra-oxy-ethyl-diphenyl Tetra-acetyl derivative C₁₂H₃Et(OAc), [138°] Formed from the tetra-ethyl derivative by successive treatment with HIAq and Ac₂O (Herzig, M 11, 418) Needles (from alcohol)

Tetra-ethyl derivative C₁₂H₃Et(OEt), [92°] A product of the action of EtI and alcoholic potash on tetra oxy diphenyl (Herzig, M

11, 417) Plates, v sol alcohol

OXY-ETHYL-PHTHALIMIDE C10HoNO, te. C.H. (CO), N CH, CH, OH [127°] Formed from bromo-ethyl phthalimide and KOHAq (Gabriel, B 21, 571) Needles or plates, sol hot water

Phenyl derivative C.H. (CO)2N C.H. (OPh [180°] Formed from PhOC2H, Br and potas sum phthalimide (Schmidt, B 22, 3255) On warming with potash it yields the acid CisHisNO.

p-Tolyl derivative [135°] Yields a di nitro derivative [88°] (Schreiber, B.

24, 190)

OXY ETHYL PIPERIDINE C,H,,NO C₅H₁₆NC₂H₄OH (199°) Formed by heating piperidine with ethylene chlorhydrin (Ladenburg, B 14, 1876) Liquid, sol water ---

B'HAuCl, plates
Phenyl acetyl derivative C15H21NO2 Oil, formed by heating phenylacetic acid with oxyethyl piperidine and HCl—B'HAuCl, [c 100°]—B'HI—B'HI, Brown needles

Benzoyl derivative C₁₄H₁₈NO₂—B'HI—

B'2H2PtCl6 silky needles

Oxy-ethyl-piperidine C₅H₁₀(C₂H₄OH)N [32°] (227°) Formed by reducing oxy α ethyl pyr idine with sodium amalgam (Ladenburg, B 22, 2586) Hygroscopic mass Yields an oily nitrosamine -B'2H2PtCl8 [158°] Large crystals

OXY ETHYL PYRIDINE $C_bH_4NC_2H_4OH$ (179° at 25 mm) 8 G 2 1 1111 Formed from (a) methyl pyridine and formic aldehyde (Laden burg, B 22, 2584) Syrup, v sol water, not volatile with steam Yields vinyl pyridine on distillation -B'2H2PtCl [170°] prisms, m sol cold water

An isomeride C,H,N (CH(OH) CH, is got

by distilling barium a oxy pyridyl propionate (Hardy a Calmels, Bl [2] 48, 230)

Oxy-di-ethyl pyridine NC₅H₅Et(C₂H₄OH) (148° at 18 mm) Formed from methyl ethylpyridine (aldehyde collidine) and formic aldehyde at 165° (Prausnitz, B 23, 2725) -B'2H2PtCl [159°] Red cubes

OXY-ETHYL-PYRIDINE TETRAHYDRIDE

CH₂<0H₂ OH₃ OH₄ NH [68°] Formed heating 8-amido heptoic acid at 220° (Aschan, B 23, 3694) Plates, smelling like confine

OXY-ETHYL-PYRIDINE CARBOXYLIC ACID NC,H2Et(OH) CO2H Formed from comanic acid and ethylamine (Ost, J pr [2] 29, 380) Prisms (containing jaq), v sol water

Di oxy-ethyl-pyridine carboxylic acid NC, HEt(OH), CO, H [c 210°] Formed from ethylamine and comenamic acid (Meunel, J pr. [2] 32, 178) Prisms (containing 2sq) Coloured violet by FeCl. Reduces ammoniacal AgNO. Ac2O at 160° forms acetyl ethyl pyromeconamic

acid C₂H₁₁NO₂ whence boiling water forms C,H,NO, [166°]

Ethyl ether Eth'. [115°] Needles (from water) — Eth'. HCl — Ba(C. 1.Et.NO.). needles OXY ETHYL-QUINAZOLINE DIHYDRIDE

C,H, < Benzylene ethyl urea [95°] Formed from w oxy-tolyl-ethyl thio-urea, alcohol, and HgO (Soderbaum a Widman, B 22, 2937). Needles (from alcohol) — B'₂H₂PtOl₆ [c 205°] — B'HAuCl, golden scales

(Py 34) OXY-ETHYL QUINOLINE

CH CH C,H, Ethyl pseudo carbostyril `NEt ĊO

Formed together with (Py 3) ethoxy quinoline by the ethylation of carbostyril (Py 3)oxy quinoline) (Friedlander a Weinberg, B 18, 1528) Glistening white needles Sl sol water, v sol other solvents Scarcely volatile with steam Dissolves in strong HCl

(Py 1, 3) Di oxy (Py 2)-ethyl quinoline Formed from chloro oxy ethyl quinoline and HCl (Rügheimer a Schramm, B 21, 301)

Prisms, v e sol alcohol
DI OXY-ETHYL ISOQUINOLINE

 $C_6H_4 < \stackrel{CH_2\cdot CO}{\sim}_{NEt}$ [105°] Formed by distil ling o carboxy phenyl acetic acid with ethyl amine (Pulvermacher, B 20, 2493) Needles, v sol alcohol With diazobenzene chloride it yields CoHoONEt N2HPh [139°]

Di-oxy di ethyl-isoquinoline

C,H,CONH [144°] Formed from di oxy isoquinoline (vol 1 p 706) NaOEt and EtI (P) White plates With alcoholic potash and Etl it produces di-oxy tri ethyl-isoquinoline C_cH₊C^{CEt}₂CO_{NEt} [50°] (309°)

(Py 8, 2) OXY ETHYL-QUINOLINE DIHY DRIDE C.H. CH. CHEt Ethylhydrocarbo styril [88°] Formed from phenyl valeric acid by nitration and reduction (Baeyer a Jack son, B 13, 119) Crystals Occurs also in an

unstable modification [76°] PCl_s gives chloro ethyl quinoline and C₁₁H₁₁NO [168°]

 (B^2) Oxy (Py 4) ethyl quinoline tetrahy dride Methyl derivative C₁₂H₁,NO Ethyl-thalline (287°) Formed from thallin and EtI (Skraup, M 6, 779) Thick liquid —B'HCl — [133°] —(B'ÉtCl)₂PtCl₄ orange needles $\mathbf{B}'\mathbf{EtI}$

(B 4) Oxy-(Py 4) ethyl-quinoline tetrahy de CH CH—C CH₂ CH₂ [76°] Pre dride pared by heating (B 4) oxy quinoline tetra hydride with EtI or EtBr (O Fischer, B 16, 717, Fischer a Renouf, B 17, 756, Fischer a Kohn, B 19, 1044, O J 49, 508) Monoclinic prisms or tables, sol alcohol and ether, sl sol Monoclinic water FeOl, colours its alcoholic solution brown -B'HCl Kaurene A Trimetric prisms, a b c

[160°] Prisms (from alcohol) Ethyl ether O.H.,NO [88°] (270°). Formed from the ethyl ether of (B 4) oxy-quinoline tetrahydride and EtBr at 180° Silky plates, insol water.—B'EtI. [1870] Prisms -

= 595 1 957, v sol water Febrifuge -B'EtI

B',Et,PtOl, [188°]
Acetyl derivative C,,H,4AcNO [64°].

OXYGEN 708

(B. 1) Oxy (Py 4) ethyl-quinoline tetrahydride CH C(OH) C SH, CH₂ . [78°] Formed by ethylating the corresponding oxy-quinoline tetrahydride (Riemerschmied, B 16, 724) Crystals, sol alcohol -B'HCl aq

(Py 3) OXY-(Py 2) ETHYL-QUINOLINE-DIHYDRIDE (Py 2) CARBOXYLIC ETHER CH₂ CEt CO₂Et

(?)C₆H₄< [114°] Obtained `N--Ċ(OH)

by reduction of o nitro benzyl ethyl-malonic ether with zinc and acetic acid (Lellmann a Schleich, B 26, 440) Color OXY-ETHYL SUCCINIC Colourless silky needles ACID ×C,H,O,

-BaA"3aq -CaA" 3aq -Ag,A" Anhydride C.H.O. s.s CHMe COCO CH2
CH(CO2H) Methyl paraconic acid [84°] Formed from aldehyde, succinic acid, and Ac2O (Fittig a Frankel,

A 255, 17) Small plates — BaA', 31aq

CaA', 21aq -AgA' Reference - TRI CHLORO OXY-ETHYL-SUCCINIO

DI OXY DI ETHYL SULPHIDE

S(CH₂CH₂OH)₂ Formed from ethylene chlorhydrin and aqueous K₂S (V Meyer, B 19, 3259)
Syrup With PCl₃ it yields S(C₂H₄Cl)₂ whence
K₂S yields insoluble C₄H₄S₂. A soluble C₄H₄S₂

1s formed from C.H. (SNa), and ethylene bromide OXY ETHYL p TOLUIDINE C.H., NO re C.H., NH CH., CH., OH [37°] (287°) Formed Formed from p-toluidine and ethylene oxide (Demole, B 7, 635, A 173, 123) Crystals, sol water -B'₂H₂PtCl₄ [148°] -B'₂H₂SO₄ [111°] - B'₂H₂C₂O₄ [122°]

Di-oxy di-ethyl p toluidine C,H,N(C,H,OH)2.

(389°) —B' H₂PtCl,

OXY-ETHYL UREA p-Tolyl-derivative NH, CO NH C.H,OC,H, [158°] Formed from tolyloxyethylamine hydrochloride and potassium cyanate solution at 100° (Schreiber, B 24, 193)

OXY-FLAVOLINE v FLAVENOL OXY-FLUORENE CARBOXYLIC ACID

C.H. $C_0^{\circ}\overline{H}_3^{\circ}(CO_2H)$ > CH(OH)[203°] Formed by reducing diphenylene ketone carboxylic acid with zinc dust and ammonia (Graebe, A 247, 283)

Crystals (from hot water or benzene)

OXYGEN O (Older names were vital air, pure air, dephlogisticated air) At w 1596 Mol w 31 92 Boils -181 4° at (v infra) 740 mm (Olszewski, W 31, 58) Has not been solidified (v infra) SG (liquid, compared solidined (b 1972) SG (liquid, compared with water at 4°) 899 at -130° (Wroblewski, W 20, 860), 7555 at -129 6°, 8788 at -139 3°, 8544 at -137 5°, 8772 at -139 4°, 124° at -1814° [=b p] (Olszewski, M 5, 124, W 31, 58), Wroblewski (Lc) gives SG for temperature from -118° to -200° as -1212 0.004871, pages T. -2882. $= 1212 + 00428T - 0000529T^2$, where T = absolute temperature SG (gaseous, at 3000 atmos. referred to water =1) 1 1054 (Amagat, C R 107, 522) Critical temp c -118°, critical pressure c 50 atmos VD 1596 (v infra) S.H p (equal weight of water = 1) 21751 from 18° to 207° (Regnault, Acad 26, 1), SHv (equal wt of water = 1) 1551 (Clausius, Mechan. Warmetheorie, 1, 62) CE (21° to 98° at 760 mm) 0086748 (Jolly, P Jubelbd 82) S 0489 at 0°, 04286 at 5°, 03802 at 10°, 03415 at

15°, .03103 at 20°, 02616 at 30° (Winkler, B. 22, 1764, S is given for each degree from 0° to 30°, and the results are compared with those of Bunsen) S (alcohol, 0° to 24°) 28397 (Carus, 4 94, 184, cf Timofejeff, Z P C 6, 141) Compressibility coefficient = 00025 at 1000-1500 atmos, 00016 at 1500-2000 atmos, 000115 at 2000-2500 atmos, 000091 at 2500-3000 atmos (Amagat, C R 107, 522) O exhibits several very different emission spectra under different conditions, for measurements of lines v B AThe absorption spectrum of O at 1884 432 pressures up to 90 atmos has been examined by Liveinga Dewar $(P\ M\ [5]\ 26,286,Pr\ 46,222)$, for the absorption spectrum of liquid O v Olszewski, W A B 95 [2nd part], 257 (cf L a D Pr 46, 422, Janssen, C R 101, 649, 102, 1332, Egoroff, C R 101, 1143)

-Uncombined in the atmosphere, Occurrence of which it forms one fifth by volume Compounds of O are very numerous, and occur in enormous quantities O forms eight-ninths of water by weight, and about one half of silica, alumina, and chalk, which are the three most plentiful constituents of the solid earth, almost every widely distributed rock or mineral con tains O, the principal exceptions being rock salt, fluorspar, blende, galena, and pyrites As O 18 slightly sol in water, this gas is found uncom bined in all natural waters O is a constituent of all living tissues, according to Wurster (B 21, 1525), O₂H₂ occurs in the juices of plants According to H Draper, O occurs in the sun (Am S [3] 14, 89, cf J C Draper, ibid 16,

O was prepared for the first time by Priestley, in 1774, by heating HgO, a year later the gas was discovered by Scheele Lavoisier was the first to recognise the importance of the dis covery of O, and to study its chemical pro perties

References to older memoirs on Oxygen -Priestley, 'Experiments and Observations on different kinds of Airs' [London, 1775-1777], 2, 29, 3, 1, Priestley, 'Experiments and Observations relating to various branches of Natu ral Philosophy '[London, 1779], 1, 192, Scheele, Abhandlungen von der Luft und dem Feuer [Upsala a Leipzig, 1777], also Crell Annal 1785, 2, 229, 291, Lavoisier's memoirs appeared in Acad from 1774 to 1788, Berzelius, Lehr

buch der Chemie [3rd ed], 5, 46
Formation — The processes wherein O is formed may be divided into groups I From air -1 BaO is heated in air to dull redness, when BaO, is formed, the pressure is decreased, and the BaO. is heated, when O is evolved, and BaO remains -2 Hg is heated in air at c 300° when HgO is slowly formed, on strongly heating HgO, O and Hg are produced—3 MnO, is heated with NaOH in air, Na,MnO, and H,O are produced (4NaOH+2MnO,+O, = 2Na₂MnO₄ + 2H₂O), the product is heated to dull redness in steam, when NaOH, Mn₂O₂₀ and O are formed (2Na₂MnO₄+2H₂O = 4NaOH+Mn₂O₄+8O), by again passing air over the residue, Na₂MnO₄ is reformed (Tessié

du Motay, D P J 186, 230) -4 When air is pressed into water, more O than N is dissolved, by reducing pressure on the water O and N are evolved, by pressing the evolved gases again 704 OXYGEN

into water, again reducing pressure, and pressing the gases into a fresh quantity of water, and repeating these processes eight times, nearly pure O (about 2-8 p c N) is obtained (Mallet, D P J. 199, 112) For details of the methods for obtaining O from air v Dictionary of Applied CHEMISTEY II From Oxedes —6 Several metallic oxides give off O when heated, eg HgO, MnO₂, PbO₂, Au₂O₃, Bi₂O₃—6 When water is electrolysed, O separates at the positive electrode - 7 O is obtained by passing a mixture of H₂O and Cl through a red hot tube, the issuing gas is passed through NaOHAq to absorb HCl and excess of Cl—8 When steam is passed over CuCl₂ at 100°-200° an oxychloride of Cu is formed which is reduced to CuCl, at c 400°, with evolution of O (Vogel, W J 1861 177, Mallet, C R 64, 226, 66, 349) -9 O is obtained by the reaction of H_2O_2Aq with $Ag_2O(Ag_2O + H_2O_2 = H_2O + 2Ag + O_2) - 10$ MnO₄, PbO₂, CrO₃, BaO₂, Bi₂O₅, and other metallic peroxides yield sulphates, H₂O, and O when heated with cone H₂SO₄ -11 CO₂ is decomposed by fresh parsley, mint, and other green plants, when the plant is placed in water sharged with CO₂ and exposed to direct sun III. From compounds other than oxides -12 KClO, is heated, either alone or mixed with MnO₂ or Fe₂O₃—13 CaCl₂O₂ is heated, when CaCl₂ and O are formed, or dry Cl is passed over CaO heated to redness— 14 Cone HNO, is dropped into a red hot Pt flask , $2HNO_1 = H_2O + O + 2NO_2 - 15$ Conc H_2SO_4 is dropped on to red-hot Pt, or on to redhot bricks, the gases produced are passed through milk of lime, $H_2SO_4 = H_2O + SO_2 + O$ (Deville a Debray, C R 51, 822) -16 By strongly heating dry ZnSO, O and SO, are evolved and ZnO remains (D a D, l.c)— 17 Ba(NO₃)₂ yields O, mixed with N, when strongly heated —18 A mixture of O and N, containing about 60 p c O is obtained by heat ing NaNO, with two parts dry ZnO (v Pepper, C N 6, 218)—19 Cone H₂SO₄ is heated with K₂Cr₂O₇ or KMnO₄, sulphates of K and Cr (or Mn) and H₂O are formed and O is evolved— 20 A fairly cone solution of bleaching powder is heated with addition of a small quantity of a salt of Co, Co2O3 is formed (by the action of the CaO on the Co salt), and this is probably oxidised to CoO, which is again reduced to Co₂O₃ with evolution of O (Winkler, J pr 98, 340, Fleitmann, A 134, 64, Reinsch, Z [2] 2, 31, Böttger, J pr 95, 309, 375, Stolba, J pr 97, 309) A modification of this process consists in passing Cl into warm thick milk of lime containing a little Co 2NO, (W, l.c)

Preparation —1 Pure KClO₂, which has been fused, is well mixed with c half its weight of pure dry MnO₂ and the mixture is heated in a flask of hard glass to c 210°–220° As the O thus obtained contains a little Cl, the gas is passed through NaOHAq or milk of lime. It is then dried by H₂SO₄, and passed in a rapid stream through a glass tube heated to redness After a time the stream of O may be allowed to alacken, and the glass tube need not be kept hot. The rapid stream of O, passing through the hot tube, washes out the last trace of air, which very obstinately adheres to glass at ordinary temperatures (Houzeau, C. R. 70, 39). Any

ozone present is also decomposed. The small quantity of air which adhe.es to the glass may also be removed, according to Ilosva (Bl [3] 2, 734), by passing the O over 2t foil at 280°-250°, or Pt black at c 250°, whereby combination of O with the N present occurs, with formation of nitrites and nitrates, which may be absorbed in NaOHAq The Pt loses the power of inducing the combination of N and O after a time, but regains this power when heated in a stream of H at c 250° (I, lc) If the O is required quite dry, it is passed through cone boiled H₂SO, and then over a long layer of P₂O, garding the part played by MnO, and other sub stances in causing O to be evolved from KClO, at temperatures lower than that at which this salt gives off O when heated alone, v Hornsby, Ph Wiederhold, P 116, 171, 118, 186, Baudrimont, J Ph [4] 14, 81, 161, Krebs, Z 6, 243, Mills a Donald, C J 41, 18, Mills a Stevenson, C J 41, 23 -2 Pure MnO, is heated to full redness in a hard glass tube, the gas is passed through milk of lime to absorb CO₂, then over Pt black at c 250° to cause combination of N (which is generally present) with O, then through NaOHAq to absorb nitrites and nitrates pro duced, and the O is then dried by cone H2SO, CaCl2, and P2O. It is difficult to obtain O by this method quite free from every impurity -3 Bottger (J pr 103, 316, 107, 48) says that pure O is obtained by gently heating KMnO,, or by the reaction of dilute HNO, Aq, SG c 1061 with a mixture of PbO2 and BaO.-4 Fairly pure O may be obtained in a regular stream, at the ordinary temperature, by compressing into small cylinders a mixture of two parts BaO, one part MnO2, and one part CaSO4, and acting on these, in a Kipp's apparatus, with HClAq, S G 12, diluted with an equal volume of water (Neumann, B 20, 3058)

Properties -A colourless, odourless, taste Condensed to a liquid at very low less gas temperatures and great pressures Liquid O is bright blue when viewed in layers 30-40 mm thick (Olszewski, W 42, 663) Pietet supposed that O was solidified when pressure was sud denly reduced, and the liquid was allowed to issue into the air (C R 86, 37), but, according to more recent experiments by Wroblewski a Olszewski (C R 100, 350, 979), solid O has not been obtained Light appears bluish when ob served through liquid O, or through a column of the gas very strongly compressed (Liveing a Dewar, P M [5] 26, 286) One litre O at 0 and 760 mm weighs 1 424488 grms at the lati tude of 45°, multiplying mean result of Reg nault (Acad 21, 158) and Jolly (W 6, 520) for weight of one litre H by mean SG of O, re ferred to H, obtained by Scott and Rayleigh (v 37, 418) The atomic volume of O

 $\left(\frac{\text{At weight}}{\text{S G of liquid}}\right)$ is c 14 (v Wroblewski, C R

102, 1010) The atomic volume of O in compounds varies according to the number of atoms with which the O is directly united, and perhaps to a small extent according to the nature of these atoms Kopp gives 12 2 for O and 78 for O EVECTOR VOLUMES, vol 1v p 498) The effect of the atom of O on the magnetic rotatory

power of O compounds is not yet determined with certainty (Perkin, C.J 45, 558, v Physical Methods, section Optical). O is absorbed by molten Ag or Pt, and given off again as the metal solidifies O is also absorbed by charcoal One voi cocoa nut charcoal absorbs o 18 vols O at 0° and 760 mm. (Hunter, P M [4] 29, 116, v also Saussure, G A 47, 113) According to Angus Smith (Pr 28, 322), the vol of O absorbed by C is eight times that of H under the same conditions O absorbed by charcoal brings about oxidation of H_2S , PH_1 , C_2H_4O , &c, fairly rapidly (Calvert, C J [2] 5, 293, cf Carbon, vol 1 p 686)

O is the most negative of the elements except F It combines directly with all elements except F, Cl, Br, I, Au, and Pt At least one binary compound of O with each element, except F and Br, is known Compounds containing O exhibit the same diverse properties The oxides of the positive elements, as a class, are basic, and those of the negative elements are acidic (v Oxides, p 658, Anhydrides, vol 1 p 267, Base, vol 1 445) O is a constituent of the greater number of acids, the compounds of O with H and non metallic elements are acids When H is combined with one of the less positive metals and a relatively large quantity of O, the compound so produced is generally an acid (v Acids, vol 1 p 47) The process of combining O with another element or with a compound is called oxidation (v Oxidation, p 657, cf Deoxidation, vol 11 p 377) When the process is attended with the production of so much heat that the products become self luminous, it is called combustion (v Combustion, vol ii p 241, cf Flame, vol 11 p 549) O is more closely related chemically to S, Se, and To than to the other ele ments It belongs to Group VI, which con tains the even series elements O, Cr, Mo, W and U, and the odd series elements S, Se, and Te (v Chromium group of Elfments, vol 11 p 168, and Oxygen group of EIEMENTS, this vol O exhibits allotropy, the allotropic infra) modification is called Ozone (v art Ozone)

Atomic weight of orygen - The value 16 01 was obtained by Berzelius and Dulong in 1819, by burning H by CuO and weighing the water formed (4 Ch 15 386) In 1842 Dumas by the same method, arrived at the number 1598 (4 Ch [3] 8, 189) In the same year, Lrdmann a Marchand conducted very carefully a series of five experiments by the same method, their mean result was 16 005. Ostwald (Lehrbuch der Allgemeinen Chemie, 1, 43) shows that the value 15 84 is obtained from Stas's experiments on the ppn of NH ClAq by Ag In 1805 Gay-Lussac a Humboldt (G A 20, 38) determined the ratio in which H and O combine, by volume, Using the values for SG of these to be 2.1 gases obtained by Biot a Arago, the atomic weight of O became 151 If Regnault's more accurate determinations of SG of H and O are made use of, and it is assumed that H and O combine in the ratio 21 by volume, then the atomic weight of O becomes 15 964 In recent years Scott has made a series of direct determinations of the relative densities of H and O (Pr 1887 898, B A 1887 668; Pr. 42, 896, N 37, 439) Keiser (B 20, 2323, Am 10, 249) caused Pd to occlude H, and then drove out the Vol. III

H over hot CuO, and weighed the water pro duced In this way a direct weighing of the H burnt was obtained Keiser's final value for O was 15 9492 Cooke a Richards (Am 10, 81) weighed H in a large balloon, and then burnt it to H₂O, they obtained O=15 953 Lord Ray. leigh, in 1888, pointed out a source of error in all experiments wherein a gas is weighed by pumping the air out of a glass globe, and thus allowing the gas to enter (the error is due to the shrinkage of the globe when evacuated) From his own experiments, Rayleigh gave $O=15\,884$ (Pr 43, 356), and applying his correction to Scott's most carefully determined values (Pr 42 396), he obtained the value 0 = 15912a Richards applied Rayleigh's correction to their experimental data, and arrived at the conclusion that O = 15 869 (Am 10, 191) The mean of the results obtained by directly weighing H and then burning it to H₂O is 15 888 The most probable value obtained by weighing H by occluding it in Pd, driving out by heat, and weighing Pd before and after, is 15 9492 The mean of the values obtained by burning H to H2O, weighing O by loss of weight of CuO, and determining H by difference between weights of H₂O and O, is 15 992 For a criticism of the methods and results up to 1885, v Ostwald's Lehrbuch der All gemeinen Chemie, 1,41 As the atomic weights of many elements are determined by directly re ferring them to O, some chemists take the atomic weight of O as 16 (H thus becomes a little more than 1) Most chemists at present take 0 = 15.96, which is the value used in this Dictionary

Reactions and Combinations -The reactions and combinations of O are too many to be described here, it must suffice to indicate them in a general way Reference should be made to the various elements and compounds for details 1 All non metals, except F, Br, Cl, and I, combine directly with O, compounds of all, except F and Br, with O are known -2 All metals, except Au and Pt, combine directly with O, com pounds of all with O are known -8 Many lower oxides are changed to higher oxides by heating in O, e q BaO, Bi₂O₂, NO, P₂O₃, PbO, FeO, many other lower oxides form higher oxides when O is produced in contact with the lower oxides (cf Oxidation, p 657, and Oxides, p 658) -4 In numerable compounds are decomposed by O, with formation of more oxidised compounds, eg NH, Aq, H, S, PbS, and Na, S, O, Aq, with many compounds O combines directly, eg P,O, HNO,Aq, SO,Aq, NO

Certain oxidations do not occur when very dry O is heated with the substance to be oxidised after it has been thoroughly dried (v Carbon, vol 1 p 687, Carbon monoxide, vol 1 p 690, v also Phosphorus, Sulphur)

Ditection of free oxygen — Uncombined O changes an alkaline pyrogallol solution to dark brown, white indigo becomes blue, NO combines with O to form red brown NO₂, easily soluble in water, CrCl₂Aq rapidly absorbs O, changing from blue to green (for preparation of CrCl₂Aq, v Nitrogen, Preparation NO 1, p 557)

M M P M

OXYGENATED WATER An older name for Hydrogen dioxide (q v, vol 11 p 722)
OXYGEN GROUF OF ELEMENTS Oxygen.

OXYGEN GROUP OF ELEMENTS Oxygen was allphur, selemon, and tellurum Oxygen was Z Z

prepared by Priestley in 1774; sulphur has been known from early times, selemon was discovered by Berzelius in 1817, tellurium was found by Klaproth, in 1798, in gold ore from the Subengebirge The name oxygen was given by Lavoisier to express the fact that many compounds of this element are acide, the word sulphur is supposed to be derived from sal = salt and $\pi \hat{\nu}_p$ = fire (burning salt or stone), the name tellurium is derived from tellus = the earth, selemon received its name from $\sigma \epsilon \lambda \hbar m$ = the moon, because of its association with and likeness to tellurium. The following table presents some of the chief properties of the four elements.—

The elements S, Se, and Te show very distinct resemblances in their caemical properties All form hydrides MH₂, which are gases at ordinary temperatures, SH₂, and SeH₂, in water redden litmus, and react as very weak acids. TeH₂ is not acidic, these hydrides are decomposed by heat, stability in this respect decreasing as at w of M increases. These hydrides are produced by passing H over molten S, Se, or Te, also by reacting on various sulphides, selenides, and tellurides, with dilute acids. The hydride of O, viz OH₂, is analogous in composition, and is formed similarly to those of S, Se, and Te, OH₂ is neutral H₂O, and H S₂ are also similar in composition and many pro-

	Oxygen	SULPHUR	SELENION	Tellurii m
Atomic weights	15 96	81 98	788	125
Molecular weights	81 92 (47 88 as ozone)	63 96 (? 191 88 at lower temps)	157 6 (? 236 4 at c 800°)	250

One or more compounds of each element have been gasified, specific heats of solid S, Se, and Te have been determined directly

		• • • • • • • • • • • • • • • • • • • •		•
Melting points (approx)	(not solidified)	112°_117°	c 200°	455°
Boiling points (approx)	-181 4° at 760 mm	44 9°	680°	below 1400°
Spec grav. (approx)	1 12 (liquid at BP)	1 96-2 05	4 8-4 8	62
Atom weight Spec grav (approx)	188	16	17 5	20
Occurrence and preparation	Very large quanti- ties of O occur un- combined in air, O is a constituent of almost all rocks and minerals, and also of all living organisms, iforms §ths of water	In large quantities in Sicily, Spain, &c, sulphides and other Scompounds are common minerals, Scompounds are found in many living organisms	small quantities,	Uncombined, also in combination with Au, Pb, S, Sb, Bi, &c, but in very small quantities
		Prepared by refining crude sulphur, also by roasting various sulphides in ab- sence of air	H ₂ SeO ₂ Aq, also by adding HClAq to	
Physical properties	A colourless, odour- less gas, bluish when much com- pressed, con- densed to a colour- less liquid, appear- ing blue in thick layers, at great pressures and low temperatures, has not been solidified.	A yellow, brittle crystalline, solid, also a plastic semi-fluid, amorphous mass Very bad conductor of electricity.	also an amorphous, vitreous, grey-	metal like, crystal-

	OXYGEN	SULPHUR	Sele/103	TELLURIUM
Chemical properties	with all elements except F, Cl, Br, I, Au, and Pt, oxides are known of all elements except F and Br Com- pounds exhibit very different pro-	ments Sulphides are basic, or acidic, or neutral, according to nature and relative quantity of element combined with S S is a constituent of several acids H ₂ S is fee-	several elements are known, they re- semble sulphides H_Se is very feebly acidic H_SeO, and H_SeO, are much weaker acids than H_SO, and	pounds not studied very fully) Bi- nary compounds resemble those of Se H ₂ Te is not acidic TeO ₂ and

Se.H2 and Te2H2 have not been preperties pared Binary compounds of S, Se, and Te with metals are analogous in composition to the Chlorides of the form MCl2 metallic oxides are known, M = O, S, Se, Te, no compound of S, Se, or Te analogous to O₂Cl is known, nor has a compound of O and Cl analogous to SCl,, SeCl, and TeCl, been obtained The stability of the chlorides towards heat increases in passing from O to Te The oxides of S, Se, and Te-MO, and MO,-are acidic (SeO, is not known), acidity decreasing rapidly as at w of M increases, TeO, is scarcely acidic, but a corresponding acid H₂TeO, exists, TeO, combines with some strong anhydrides to form compounds of the type of salts The oxyacids H,MO, and H,MO, are analogous in composition, but the acids of S are very much stronger than those of Se or Te, those acids yield oxychlorides, MOCl, and MO₂Cl₂, by reacting with PCl, Many other oxyacids of S are known

The elements of the O family exhibit allotropy, O and S in a very marked way, Se less markedly, and Te only slightly. The allotropic forms of O exist as gases, their molecular formulæ are O₂ and O₃, the allotropic forms of S, Se, and Te are known with certainty only as solids. It is doubtful whether molecules of S or Se, other than S₂ and Se₂, exist as gases through any considerable range of temperature, the only molecule of Te existing as a gas is Te. The mol w of S in solution is certainly greater than S₂, and probably varies according to the

The elements S, Se, and Te form the oddseries members of Group VI, of which group O forms the first even series member, the other even series members are Cr, Mo, W and U All the members of Group VI are characterised by forming acidic oxides MO,, as the at w increases these oxides become less soidic. Only the odd series members, and O, form hydrides All form chlorides MCl, the stability of which towards heat increases from O to U, the higher members also form several other stable chlorides Group VI falls into two families, (1) S, Se, Te (11) Or, Mo, W, U, O is the typical element of the group (cf. CHROMIUM GROUP OF ELEMENTS, vol 11 p 168, v. also Oxxonn, Sulphum, Sele-MION, TELLURIUM). M. M P. M.

a-OXY-GLUTARIC ACID

CO₂H CH(OH) CH₂CH₂CO₂H Glutane acid [78°]? (M) Formed from amido glutane acid and HNO₂ (Ritthausen, J pr 103, 239, Markownikoff, A 182, 348) Occurs in beetroot molasses (Lippmann, B 15, 1156) Readily yields the lactonic acid —CaA" ½ aq —MgA" 4aq —PbA" ½ aq —ZnA" 3aq —Ag₂A" ½ aq

Lactonic acid C.H.O. i.e.

CH₁

CH₂CH CO H

CH CO H

CH CO H

needles (Wolff, A 260, 126) — CaA', 2aq —

BaA', — ZnA', 2aq Yields glutaric acid [98°]

on reduction by HI.

S-oxy-glutaric acid Methyl derivative CO₂H CH₂CH(OMe) CH₂CO₂H Formed by oxidising di allyl-carbinol with 5 pc solution f KmO₄ (R₁sbinin, J pr [2] 23, 274) Extracted with ether (v Oxyryrotarranc acid)

Salts - CaA" (at 100°) Syrup, covered by crystalline crusts -BaA" -Ag₂A" Prisms

a.B-Di-oxy glutaric acid
CO.H. CH., CH.(OH) CH.(OH) CO.H. [156°]
Formed by boiling glutaconic acid-di bromide
with water and CaCO. Needles (from water),
or six sided tables (from alcohol) V e sol.
water, v sol alcohol Its Ca salt is easily
soluble (Kiliani, B 18, 2517)

αγ-Di-oxy glutaric acid
CO₂H CH(OH) CH₂CH(OH) CO₂H Formed by
heating the di oxy-propane tri-carboxylic acid,
which is obtained by oxidising isosaccharic acid
with HNO₂ Colourless prisms V e sol water,
v sol alcohol, al sol ether Its Ca salt is
sparingly soluble (Kiliani, B 18, 2516)
Tri-oxy-glutaric acid C₂H₂O₇ [127°]

Tri-exy-glutaric acid C,H,O, [127°] Formed from arabinose or sorbin by oxidation with HNO, (S G 1 2) (Kiliani, B 21, 3006, 3276)—K,A" monoclinic plates

OXYGUANIDINE Obtained by boiling cyanamide with alcoholic hydroxylamine hydrochloride (Pretorius a Seidler, J. pr. [2] 19, 899).

—(ON,H,O),H,PtCl, ruby-red prisms
ONY-H,EMOGLOBIN v H,mootlobin,
ONYHALOID COMPOUNDS Compounds of
F, Cl, Br, or I, with O and another element.
Onyhaloid compounds of non-metals are often
formed by reacting with PCl, PBr, or PI, on
onyacids, e.g. SO,Cl, from SO,(OH); they are
also produced sometimes by heating together as

oxide and chloride, e g BOCl by heating B2Os with BCl, sometimes the halogen is directly combined with an oxide, e g COCl, and NOCl by combining CO and NO with Cl, and BOCl, by heating Cl with B₂O₃ mixed with C Metallic oxyhaloid compounds are formed by decomposing the haloid compounds of the metals by water or steam, by heating together oxides and haloid compounds, and in some cases by the incomplete ppn of haloid compounds in solution by alkalı Non metallıc oxyhaloid compounds are decomposed by water to haloid acids and other oxides or oxyacids of the non metal present Some metallic oxyhaloid compounds are also decomposed by hot water to haloid acids and metallic oxides, in this respect the oxyfluorides are the most stable, and the oxylodides, as a class, are more stable than the oxybromides and The oxyhaloid compounds of H oxychlorides are acids All elements form one or more oxy haloid compounds A metal which readily forms many oxyhaloid compounds generally forms one or more oxides with acidic reactions, and is otherwise more or less non metallic in its chemi MMPM cal properties

DI-OXY-HENDECOIC ACID C11H20(OH)2O2 [85°] Formed by the oxidation, in alkaline solution, of hendecenoic acid derived from castor oil (Hazura a Grussner, M 9, 952) Needles, sol hot water

OXY HENICOSOIC ACID

 $\mathbf{C_{19}H_{88}(CH_2OH)(CO_2H)}$ [1035°] Occurs in the soda soap from carnauba wax $(q \ v)$ Crystalline powder (from petroleum), sl sol alcohol, m sol isobutyl alcohol (whence it separates as a jelly) (Starcke, A 223, 310) As its alcoholic solution is not ppd by acetate of Mg, Cu, or Pb, it is possibly a lactone C₁₉H₃₈< CH₂>O Heated

with soda lime it splits off H2, forming a di-

basic acid $C_{19}H_{38}(CO_2H)_2$ [90°]

PENTA OXY HEPTANE The oily anhydride C,H11(OH)2O is formed by the action of HOCI followed by KOH on di allyl carbinol (Reformatsky, J R 21, 295) The acetyl derivative C,H₁₁(OAc)₅ (169 5°) S G ² 919 is described by Saytzeff (A 185, 129)

OXY-HEPTANE PHOSPHONIC ACID

C,H₁,PO₄ is C₆H₁₃ CH(OH) PO(OH)₂ [185°] Formed from enanthol and PCl₃ followed by water (Fossek, M 7, 27) Monoclime tables $a \ b \ c = 1\ 844\ 1\ 1\ 957$, $\beta = 74^{\circ} - \text{CaA''}$ The compound $(C_6H_{18}\ \text{CH}(\text{OH}))_2\text{PO}\ \text{OH}\ [160^{\circ}]$

is formed by heating cenanthol with hypophos phorous acid (Ville, C R 109, 72) It yields the salts BaA', 3aq, PbA', 3aq, KA' 4aq, and (C.H.,CH(OAc)),PO.H [94°]

OXY-HEPTENOIC ACID

CHMe(OH) CH(C₃H₅) CO₂H Formed from allyl-acetoacetic ether and sodium amalgam (Zeidler, A 187, 45) water —BaA'₂, —Zn(OH)A Syrup, miscible with

Oxy-heptenoic acid Natrale

CHEt CMe OH(OH) CN Formed from methylethyl-acrolein and HCy (Johanny, M 11, 401) Converted by hydrochloric acid into the amide CHEt CMe CH(OH) CONH, [101°] The nitrile yields an only acetyl derivative (114° at 22 mm), ▼ sol ether

Oxy-heptenoic lactone v Mesitonic Acro

OXYHEPTIC ACID C,H107, gaq? [1850] product of the action of bromine, followed by alcoholic potash on isobutyl acetoacetic ether (Demarqay, C R 86, 1135) Pearly scales (from water) Yields C,H,O(OEt),NH, ? [87°] a-OXY-HEPTOIC ACID C,H,1,O, 16 Pr CH, CH, CH(OH) CO,H. [60°] (Helms, B 8, 1167), [65°] (Ley, J R 9, 141) Formed by heating aqueous potassium bromo heptoate at 140° Prisms — MeA' [160°-165°]

Amide [147°] Hexagonal tables a Oxy heptoic acid C₅H₁₁ CH(OH) CO₂H [60 5°] Formed from its ether, EtA' (203°), which is produced, as well as t e ethyl derivative thereof C₃H₁₁CH(OEt) CO₂Et (c 224°) by the action on oxalic ether of zinc and isosinyl 10dide at 100°, followed by water (Frankland a Scales —BaA'2 — CuA'2 Duppa, Pr 14, 191)

β Oxy-heptoic acid CHMe, CH(OH) CMe CO₂H [112°] The chief product of the action of sodium on isobutyric ether (Hantzsch, A 249, 60) Silky needles, m sol water, volatile with steam -BaA', 41aq Ethyl derivative of the ethyl ether Pr CH(OEt) CMe, CO,Et (181° cor) Oil

β Oxy heptoic acid CHMe(OH) CMe EtCO.H Formed by reducing CH, CO CMeEt CO2Et with sodium amalgam (Saur, A 188, 266) Syrup, v e sol water -CuC, H12O, -AgC, H12O, plates, m sol hot water

β Oxy-heptoic acid CMePr(OH) CH CO,H Formed by oxidising CMePr(OH) ClH₃ with KMnO₂ (Semljanitzin, J pr [2] 23, 267) Syrup —CaA', (at 100°) —BaA'₂ —AgA' prisms g Oxy-heptoic acid CEt₂(OH) CH₂ CO₂H

[39°] Formed by oxidising CEt₂(OH) C₃H, with KMnO. (Schirokoff. J pr [2] 23, 201) Thia KMnO₄ (Schirokoff, *J pr* [2] 23, 201) Thi needles — LiA'aq — CaA'₂aq — BaA'₂2aq — PbA'₂2aq S 6 at 19° — CuA'₂5aq — AgA'

γ Oxy-heptoic acid CHPr(OH) CH, CH, CO,H Syrup -BaA', -AgA' curdy pp

Lactone Pr CH CH2 CH2 CO Formed by the action of HI and P on the hexa oxy heptoic acid obtained from dextrose (Kiliani, B 18, 3066, 19, 1128) Obtained also from propyl paraconic acid Pr $CH < CH(CO_2H) > CH_2$ distilling, converting the resulting CHPr CH CH₂ CO₂H into γ bromo heptoic acid, and boiling this with water (Fittig, B 20, 3180,

A 255, 76) An isomeric lactone (220° cor) is obtained

in like manner from levulose

γ Oxy-isoheptoic acid CHPr(OH) CH2 CH2 CO2H Very unstable — BaA'2 -AgA'

Lactone $C_7H_{12}O_2$ (225° uncor) S 3 in the cold Formed from γ brome isoheptoic acid and also by distilling isopropyl paraconic acid (Fittig a Zanner, A 255, 94) Liquid, volatile with steam

γ Oxy-heptoic acid —BaA'2 —AgA' Lactone C,H₁₂O₂ [11°]. (220° 1 V) S 8 3 at 0°. Formed from tetracrylic acid and cold HBrAq (Fittig a Krafft, A 208, 86) Liquid γ-Oxy-heptoic acid Lactone

 $CHMe < \begin{array}{c} CH_2 CMe_2 \\ O - CO \end{array} [52^{\circ}]$ (86° at 15 mm). Formed by reducing β -acetyl valeric acid with sodium amalgam (Anschutz, A 247, 107) Large | amalgam (Lipp, B 18, 3282) Thick colourless crystals

γ Oxy-heptoir acid

CH₃ CH(OH) CH₂ CHEt CO₂H Formed by re ducing β -acetyl valeric acid with sodium amalgam (Young, C J 43, 173, A 216, 38) The iree acid changes quickly, especially on boiling, to the lactone —BaA'₂ —AgA' curdy pp

Lactone CH, CH CH2 CHEt $(219.5^{\circ}$

1 V) SG 16 992 Liquid, m sol water solution saturated at 0° becomes turbid at 17°

and clear agean at 95°

Hexa-oxy-heptoic acids are formed from levulose, dextrose, and galactose by successive treatment with HCy and alkalis (Kiliani, B 18, 3066, 19, 767, 22, 521) The free acids change to lactones C,H12O, The hexa oxy heptoic acid from galactose crystallises in needles [145°] and

forms the salt KA' aq DI-OXY-HEPTYLENE C,H₁₂(OH)₂ (1956° cor) VD 636 A product of the distillation of resin (Morris, O J 41, 169) White Forms a hydrate C,H14O2 aq [c 106°]

A cetyl derivative C,H₁₂(OAc)₂ [69°] TETRA - OXY - TETRA HEPTYL PHOSPHO NIUM IODIDE (C₆H₁₃ CH(OH))₄PI [122°] Formed from PH₄I and heptone aldehyde (De Girard, A Ch [6] 2, 40) Laminæ

OXY HEPTYL PYROTARTARIC ACID Lactonic acid C12H20O4 Methylhexylparaconic acid [107°] Formed from cenanthol, pyrotartaric acid, and Ac₂O (Riechelmann, A 255, 132) Plates, gol ether -BaA'₂ 3aq -CaA'₂ aq -AgA' needles (from water)

β-OXY HEPTYL SUCCINICACIDC11H20O51 e C₆H₁₃ CH(OH) CH(CO H) CH CO_.H The salts are got by boiling the malic acid lactonic acid with bases - CaA" (at 100°) -BaA'' (at 130°) -Ag₂A'

Lactonic acid

 $C_6H_{13}\,CH{<_{\rm O\ CO}^{\rm CH(CO_2H)}}{>}CH.$ Heayl paraconic

acid [89°] Formed from @nanthol, Ac.O. and barium succinate at 120° (Schneegans, A Needles, sl sol water - Ca A', 2aq -AgA', flocculent pp DI OXY HEXADECANE

C14H30(OH)2 Formed from C16H12Br, and AgOAc followed by KOH (Krafft a Grosjean, B 23, 2352)

Di-acetylderivative C₁₆H₃ (OAc)₂ [56°]

DI OXY HEXANE C.H.O. 16 CHMe(OH) CH₂ CH₂ CHMe(OH) (220° 1V) S G $\frac{9}{6}$ 976, $\frac{34}{5}$ 961 C E (0°-24°) 00064 (Soro kin, J pr [2] 23, 18) Formed from diallyl by successive treatment with HI, AgOAc, and KOH (Wurtz, A Ch [4] 3, 162) Liquid, sol water

Mono acetyl derivative (210°) Di acetylderivative C₆H₁₂(OAc), (225°) Di-oxy-hexane (207°) SG 2 9669 Ob tained from hexylene derived from mannite (Wurtz, Hecht, B 11, 1154) The correspond-

ing oxide, C₂H₁₂O (110°), is formed from C₂H₁₂OCl and KOH (Eltekoff, J R 1882, 355) Dr acetyl derivative (215°-220°) S G

Di-oxy-hexane CH, CH(OH) CH, CH, CH, CH, (OH) Hewylene 5-glycol (235° at 710 mm) S G at 0° = 9809 Prepared by reduction of aceto butyl alcohol CH, CO CH, CH, CH, CH, OH with sodium-

fluid of slight smell and bitter taste water and alcohol, more sparingly in anhydrous By heating with HCl it is converted into hexylene-5 chlorhydrin, and by prolonged action into hexylene di chloride By heating with H₂SO₄ (b5 p c) it splits off H₂O, forming hexylene 8 oxide

D1-oxy-hexane CHMe(OH) CHPr(OH) [c 0°] (207°) Formed from aldehyde, 180butyric aldehyde, and alcoholic potash (Fossek, M 5, 119, Swoboda, M 11, 389) Thick liquid, Dilute H2SO, forms, on heating, sol water (β) pinacolin $C_{12}H_{24}O_2$ (210°)

Isomeride v Pinacone

Tri-oxy hexane C.H.,O. te CH₂(OH) CH(OH) CH₂ CMe₂(OH) Heacerin (190° at 50 mm) S G 2 1 0936 Hexyl gly-

Formation—1 By addition of bromine to CMe₂(OH) CH₂ CH CH₂ and decomposition of the product with baryta (Orloff, Bl [2] 47, 167) 2 From di methyl allyl carbinol by successive treatment with HOCl and aqueous KOH, or with Br and baryta (Orloff, Bl [2] 45, 253, A 233, 351, Reformatsky, J pr [2] 31, 318, 40, 398)

Properties — Syrup, sol water and alcohol,

insol ether

Tri acetyl derivative Oil.

Tri oxy hexane CH₂(OH) CH(OH) CH₂ CH CHMe(OH) (181° at 10 mm) S G ⁹/₄ 1 1012 Formed by heating its the acetyl derivative with PbO Liquid, sol

Tri acetyl derivative C₄H₁₁(OAc), (c 283°) SG ½ 1 109 CE 000873 Formed by heating methyl butenyl carbinol (from allyl acetone) with Ac2O (Markownikoff a Kabloukoff, Bl [2] 34, 347, 37, 346, 43, 111). Heavy oil Yields an oxide C.H.O. (178°)

Tri-oxy hexane CHEt(OH) CMe(OH) CH₂OH (170°-176° at 53 mm) Formed by boiling the dibromide of methyl ethyl allyl carbinol with water (Lieben a Zeisel, M 4, 41) Liquid

Ceisel, M 4, 41) Liquia
Tri acetyl derivative (c 270°) Oil
Tri acetyl derivative (c 270°) Formed Tetra oxy hexane C₈H₁₄O₄ [95°] Formed by oxidising diallyl with KMnO₄ (Wagner, B 21, 3343) Plates, v sol water, m sol cold alcohol, insol ether

OXY HEXANE DISULPHONIC ACID C_6H , $O(SO_2H)$ Formed from methyl ethylacrolem and SO₂ at 80° (Ludwig, M 9, 667) -BaA"2aq converted by sodium amalgam in presence of acids to hygroscopic sodium oxyhex me sulphomate C.H.O(SO,Na)

OXY-HEXENOIC ACID C.H,O, A product of the action of boiling water on the dibromide of hydrosorbic acid (Fittig, A 200, 57) Liquid

CaA', 1 aq plates
OXY HEXIC ACID C.H.O. aq or C.H.O. [174°] Formed from propyl acetoacetic ether by successive treatment with Br and alcoholic potash (Demarçay, C R 88, 289) Small pearly

plates, v e sol hot water Is perhaps identical with terebic acid (Gorboff, J R 1887, 605) Reduced by Zn and H₂SO₄ to C,H₁O₄(?) [98°] Yields an amide C₁₈H₂₁O₄(NH₂)₅(?) [215°] and an amic ether C₁₀H₁₈NO₂(?) [79°] Iso-oxy-hexic soid [187°] Formed in like

manner from isopropyl-acetoscetic ether (D Reduced by Zn and H2SO, to C,H12O, (?) [113°] Yields CisH₂₁O₅(NH₂)₅(?) [240°] and another amıde $C_s\ddot{H}_7\ddot{O}(\ddot{N}\dot{H}_2)(\ddot{O}\dot{E}\dot{t})'_2(?)$ [95°]

DI-OXY-HEXINENE v DI OXY-HEXYLENE

a-OXY-HEXOIC ACID CaH12Oa 26 OH.Pr CH(OH) CO.H Leucic acid Mol w 182 [73°] Formed by the action of nitrous acid on leucine (Strecker, A 68, 55, Thudiohum, C J 14, 807, Waage, A 118, 297) Needles, v sol water, alcohol, and ether—BaA'₂ silky lamins (from hot alcohol) —CaA'₂ —CoA'₂ — CuA'₂ —ZnA'₂ aq S 33 at 16°, 5 at 100° — ZnA'₂ 2aq (Körner, G 13, 356) —AgA' orystalline pp

An isomeric or identical oxy hexoic acid [62°] is formed by the action of Na CO, on bromohexoro acid got from fermentation hexoro acid (Jehsafoff, J. R. 12, 367, Bn 1, 523) It yields the salts CaA'₂, BaA'₂, MgA'₂ 2aq, ZnA'₂ 2aq (8 ·14 at 16°, 21 at 100°), CuA'₂, and AgA' It

forms a crystalline amide [142°

[80°] α-Oxy-hexoic acid CEt₂(OH) CO₂H 8. 35 at 17 5° Formed from its ether which is got from oxalic ether by the action of ZnEt, followed by water (Frankland, Pr 12, 396, Frankland a Duppa, Pr 13, 140, A 135, 26, Geuther, Z 1867, 705, Fittig, A 200, 21) Triclinic crystals, v sol water, alcohol, and ether Yields di-ethyl ketone on oxidation -NH₄A' -BaA'₂ -BaA'₂5aq —ZnA'₂ AgA'aq needles S 33 at 16° - CuA₂-

Methyl ether MeA' (165°) SG 165 987 Ethyl ether EtA' (175°) VD 524 (calc 553) SG 187 961 Oil Formed from OOI CO₂Et and ZnEt₂ (Henry, B 5, 949)

Isoamyl ether (225°) S G 12 983

Netrele CEt₂(OH) CN Formed from COEt₂

and HCy (Tiemann a Friedlander, B 14, 1974)

a-Oxy-hexoic acid CH, Pr CH(OH) CO, H [56°] Got by saponification of its nitrile, which is formed from isovaleric aldehyde and HCy (Erlenmeyer a Sigel, B 7, 1109, Ley, B 10 231) Formed also by heating isobutyl tartronic acid at 180° (Guthzeit, A 209, 239) Plates -ZnA', 2aq S 12 at 16°

Nitrile Oil, lighter than water

β Oxy-hexoic acid CHMe(OH) CHEt CO,H Formed from ethyl acetoacetic ether and sodiumamalgam (Waldschmidt, A 188, 240) Syrup -NaA' -CuA'2 -AgA' plates

a Oxy-hexoic soid CMe, CH(OH) CO H
[88°] Formed by reducing tri methyl pyruvic acid with sodium amalgam (Glucksmann, M Monoclinic crystals -AgA

β Oxy-hexoic acid CHEt(OH) CHMe CO₂H Formed by reducing propionyl propionic acid (Hantzsch a Wohlbruck, B 20, 1320) —NaA'

y-Oxy-n-hexoic acid CHEt(OH) CH2 CH2 CO2H The salts are formed by the action of bases on the lactone The free acid quickly changes to lactone -CaA'2 -BaA2 -AgĀ'

Lactone CoH10Os to CHEt CH2 CH2 CO (220°) Formation -1 By boiling with water the brome-hexoic acid formed by the union of hydrosorbic soid with HBr (Fittig, B 13, 955, A 208, 67) —2 By heating glutaconic acid with HI and P (Kiliani a Kleeman, B 17, 1800) — 3 By reduction of metasaccharin with HI

(Kılıanı, B 18, 642) -4 By Warming hydrosor bic acid with dilute (1 1)H2SO4 (Fittig, A 256,

134)

Properties - Liquid, m sol water Volatile with steam Its aqueous solution becomes tur bid when heated to 40°, but clear again at 80° K2COs separates it from the solution HI and P reduce it to n-hexoic acid

Amide CHEt(OH) CH2 CH2 CONH2 [74°] Formed by heating the lactone with alcoholic NH, at 100° Prisms, ve sol water and alcohol,

sl sol ether

γ-Oxy-isohexoic acid

OMe₂(OH) CH₂ CO₂H Crystalline, but very unstable —BaA' (at 100°) —AgA'

Lactone C₂H₁₀O₂ (207° 1 V) Formed from terebic acid by distillation, by successive treatment with HBr and water, or by boiling with dilute H₂SO₄ (Fittig a Bredt, A 200, 58, 259, Geisler, A 208, 43, Erdmann, A 228, 181) Formed also by oxidising isohexoic acid with KMnO₄ (Bredt, A 208, 59) Liquid, v sol water Neutral in reaction Its aqueous solution becomes turbed at 35°, clear again at 80° Yields on oxidation with HNO, the acid CoH,O4 [68°], whence $CaC_6H_8O_8$ 7aq and $AgC_6H_7O_4$ Boiling NaOEt forms an anhydride C_1 $H_{18}O_3$

[106°], whence HClAq forms $C_{11}H_{20}O_{2}$ (209°) γ 0xy-hexoic acid $CH_{2}(OH)$ CH_{2} CHEt CO HFormed from CH_{2} CO CEt(CH_{2} CH OH) CO_{2} Etby boiling with baryta water (Chanlaroff, A 226, 335) Thick liquid, changing to the lactone on boiling its solution $Ba(C_0H_{11}O_5)_2$ crystals (from alcohol) $-CaA'_2 - AgA'$, needles (from water) $Lactone\ CH_2 < \begin{array}{c} CH_2\ CHEt \\ O-CO \end{array}$ (215°) S G

19 1 035 Liquid, m sol cold water γ Oxy hexoic acid

CHMe(OH) CH₂ CHMe CO₂H Formed by re duction with sodium amalgam from \$ acetyl isobutyric acid derived from a bromo propionic ether and sodium acetoacetic ether (Fittig a Gottstein, A 216, 30) Formed also by reducing saccharin or isosaccharin with HI and P (Lie bermann a Scheibler, B 16, 1821, Kılıanı, B 18, 635) —BaA'2

(206°) Lactone Liquid, sol 20 - 25volumes of water An isomeric anhydride [137°] is also formed by reducing isosaccharin

γ Oxy hexoic acid

CHMe(OH) CHMe CH₂ CO H Formed by reducing β -acetyl n butyric acid (Gottstein, A 216, 36) Yields a lactone (210°)

δ Oxy-hexoic acid

CHMe(OH) CH₂ CH₂ CH₂ CO₂H Obtained by reducing γ -acetyl n butyric acid with sodium amalgam at 30° (Fittig a Wolff, A 216, 133) When boiled with water it is partly converted into the lactone When the lactone is boiled with water it is partly conveited into the acid Equilibrium occurs with 65 pc lactone and 35 pc acid -AgA'

Lactone [19°] (c 231° 1 V) Colour-

less liquid, solidifying below 0° Miscible with water but separated by K₂CO₃

Oxy bexoic acid C₄H₁O₃ [108°]. Formed by oxidising oil of millet with KMnO, (Kassner, As Ph [8] 25, 1081) Plates, v sol water. Yields an acetyl derivative [71°]

Di-oxy-hexoic acid [141°] Formed from ethyl crotonic acid by successive treatment with bromine and with water at 100° (Fittig a Howe, A 200, 39) Trimetric prisms, a b c = 961 33 V sol water and alcohol.—CuA', 3 aq. brightblue needles

Di oxy-hexoic acid

CHMe(OH) CEt(OH) CO₂H [96°] Formed by oxidising ethyl crotonic acid with KMnO, (Fittig, B 21, 920)

D1-oxy-hexote acid

CHEt(OH) CMe(OH) CO,H [152° cor] Formed by oxidation of methyl ethyl acrolem (Lieben a Zeisel, M 4, 65) Needles or prisms — CaA', 3aq crystalline m ss

Hexa-oxy-hexoic acid C_eH₁₂O₇ Arabinose-carboxylic acid Formed from arabinose by the action of aqueous HCy, followed by saponi fication (Kiliani, B 29, 3033, 20, 339) When liberated from its salts it immediately forms the

lactone —CaA'₂ amorphous Amide Minute needles

Lactone C₆H₁₀O₆ [145°-150°] $[a]_D =$ Needles or prisms Yields metasac -548charic acid dilactone CaHeOe on oxidation by HNO₃ and n hexoic acid on reduction by HI and P

DI OXY HEXYLENE C.H1.O2 Hexinene glycol (218°-225°) Formed from epichlorhydrin and Na (Hubner a Miller, A 159, 186)

Is perhaps di oxy hexinene (Claus, B 10,556)

OXY HIPPURIC ACID C,H,NO, ve
C,H,(OH) CO NH CH, CO,H Formed from m amido hippuric acid by the diazo reaction (Griess. B 1, 190, Conrad, J pr [2] 15, 259) Needles, v sol hot water

OXY HYDRASTININE v Hydrastine

OXYHYDROANTHRANOL v OXYANTHRANOL HYDRIDE

TRI OXY HYDROBENZAMIDE v OXY BEY ZOIC ALDEHYDE

OXYHYDROBENZOIC ACID C H.O. cor] Formed from oxy uvitic acid and aqueous KMnO₄ (Oppenheim a Emmerling, B 9, 327) Needles Yields benzoic acid by potash fusion -CaA'2 3aq -AgA' v sl sol water

OXÝ HÝDRO COUMARILIC ACID v COUMA

RILIC ACID

OXY HYDRONAPHTHOQUINONE v HYDRO-AUGLONE

OXY HYDROQUINOLINE v OXY QUINOLINE HYDRIDE

OXY HYDROQUINONE v TRI OXY BENZENE OXY - DIHYDROQUINOXALINES v QUINOVALINE DIHYDRIDE

OXYHYPOGÆIC ACID C16H30O3 [34°] Formed from di bromo palmitic acid and Ag₂O White mass (Schroder, A 143, 36)

OXY-DIIMIDODIAMIDOIASTIN v ISATIN OXY IMIDO METHYL PYRIMIDINE DI

HYDRIDE C(NH) < NH CMe > CH methyl uracil [270°] Formed from guanidine, alcohol, and acetoacetic ether (Jaeger, A 262, 365) Prisms, v sol hot water Yields a dibromide [160°] MeI forms C₅H₆MeN₅O [812°], whence B'HI [212°], B'HClaq, and B'H2SO4 [270°]

[180°]. Salts -B'HCl [295°] -B'H2SO.

-B'HNO, needles

Oxy imido-di-methyl-pyrimidine dihydride C(NH) < NH COO > CMeFormed [820°]

from guanidine and methyl-acetoacetic ether -B'H,SO,. [265°] —B'HNO, [200°]. Plates OXY-IMIDO-PHENYL-PYRIMIDINE DI-

HYDRIDE C(NH) < NH CO CH. Imido phenyl-uracil [294°] Formed from guanidine Amorphous powder, insol water and alcohol

OXY IMIDO-DIPHENYL SULPHIDE

 $\mathrm{NH} < \stackrel{\mathrm{O_{c}H}}{\overset{\mathrm{I}}{\overset{\mathrm{O}}{\overset{\mathrm{O}H}}}} > \mathrm{s.}$ Formed from oxydi phenylamine by heating with S (Bernthsen, A 230, 182) Colourless mass, v sol alcohol and FeCl, forms a chocolate pp of ether $N < C_0H_0$ S, insol water

DI-OXY-IMIDO-DIPHENYL SULPHIDE $\mathrm{NH} < \substack{\mathrm{C^6H^3(OH)} > \mathrm{S}}$ Formed by reducing thionol $N < C_sH_s(OH) > S$ which is itself got

by the action of conc H2SO4 on imido diphenyl sulphide (Bernthsen, A 230, 188) Colourless needles, v sl sol water Yields a tri acetyl derivative [156°]

DI-OXY-IMIDO-PYRIDINE DIHYDRIDE v

DI OXY AMIDO PYRIDINE DI OXY DI IMIDO QUINONE

C₆(NH)₂(OH)₂O₂ Formed by oxidising tetra oxy di amido benzene by FeCl₂ (Nietzki, B 16, 2094, 18, 503) Plates, v sl sol alcohol

OXY INDAZOLE C,H,(OH)N, [215°-266°](?) Formed by boiling diazo indazole with water (Witt, Noelting, a Grandmougin, B 23, 3642) Needles, sl sol cold water

OXY-INDOLE v Oxindole

(a) OXY INDONAPHTHENE C.H.O CeH CH CH (a) Hydrindone [40°] (244°) Formed by heating o cyano benzyl acetic ether with conc HClAq (Gabriel a Hausmann, B 22, Colourless tables Conc HClAq at 100° 2018) forms (C₉H₆),, not melted at 280°

Oxim C,H,(NOH) [146°] White needles

(from alcohol), sol alkalıs

Phenyl hydrazide C₉H₈(N₂HPh) 120°] White prisms, converted by cone HClAq into C₁₅H₁₁N [235°]

References -DI BROMO and CHLORO DI- OXY INDONAPHTHENE

OXY-ITACONIC ACID C, H,O, Formed by boiling aconic acid with baryta water (Meilly, Oil -BaA" (at 160°) -Ag2A" A 171, 153)

flocculent pp

OXY-JUGLONE v JUGLONE

OXY-LEPIDINE v OXY METHYL QUINOLINE

OXY LEUCOTIN v COTOIN

OXY-LUTIDINE v OXY DI METHYL PYRIDINE OXY-MALONIC ACID v TARTRONIC ACID OXY-MARGARIC ACID C17H24O3 [80°].

Occurs in adipocere (Ebert, B 8, 775) -AgA' amorphous

OXY . TRIMELLITIC ACID C.H.O. Formed C₆H₂(OH)(CO₂H)₂ [5 4 2 1] [c 245°] by fusing sulpho trimellitic acid with potash (Jacobsen a Meyer, B 16, 192) Prisms (con taining 2aq) With HClAq at 240° it yields moxy-benzoic acid -Ba,A", 5aq small prisms.

OXY-TRIMESIC ACID C₄H₂O₇ s.s. C₅H₂(OH)(CO₂H)₁[2 5 3 1] S 5 at 10° Formed by heating [2 1]C₅H₄(ONa)CO₂Na in a current of CO₂ (Ost, J pr [2] 14, 95, 15, 302, 17, 284), and by fusing C₅H₂(SO₂NH₂)(CO₂H)₃ with potash (Jacobsen, A 206, 204) Nodules (containing act) or peedles (containing act) or peedles (containing act) or peedles (containing act) aq) or needles (containing 2aq) Decomposes at 180°—Ca₂A'''₂ 8aq —Ca(H₂A''')₂—Ba₂A'''₂ 8aq — Ag,A" Saq

Ethers Et.HA'"aq [148°] —Et₂NaA'''aq -Et.A'". [84°] -Et.NaC.H.O. prisms, insol.

OXY-MESITENE CARBOXYLIC ACID v ACETO ACETIC ACID

∞-OXY-MESITYLENE C₆H₃Me₂CH₂OH

(220°) Heavy oil (Wispek, B 16, 1577)

Acetyl derivative (230°) SG 16 109 Formed from ω-bromo mesitylene and KOAc

Isomeride v Mesitol

Di.a-oxy.mesitylene C.H.Me(CH.OH). Mes-tylenic glycol (280°) S G 25 123 S 5 S (ether) 50 Obtained by prolonged boiling of ω di chloro-mesitylene [41 5°] with water and lead carbonate (Robinet a Colson, C R 96, 1863). Liquid, with bitter taste, v sol alcohol

Dr-acetyl derivative C.H.Me(CH2OAc)2.

(244° at 120 mm) SG 20 1 12 Oil Isomeride v Tri METHYL RESORCIN Tri-ω-oxy mesitylene C₉H₉O, ι e

C.H. (CH2OH), Mesicerin Obtained by boiling tri-w bromo mesitylene with water (40 pts) and lead carbonate (Colson, A Ch [6] 6, 95) Syrup, gradually crystallising in a desiccator Sol alcohol, insol chloroform and ether

o-OXY-MESITYLENIC ACID C₂H₁₀O₃ te H₂Me₂(OH)CO₂H [5 3 2 1] [179°] Formed C₆H₂Me₂(OH)CO₂H [5 3 2 1] [179°] by potash fusion from mesitylene sulphonic acid (Fittig a Hoogewerff, A 150, 333), from mesitol (Jacobsen, A 195, 274), (a) sulpho mesitylenic acid (Remsen, Am 3, 220), and mesitylene di sulphonic acid (Barth a Herzig, M 1, 812) Jacobsen, B 11, 2055) Prepared from m xylenol, Na, and Co₂ (Jacobsen, B 14, 44) Needles (from dilute alcohol) FeCl₃ colours its solution blue — NH₄A'—KA'—CaA'₂ 5aq—BaA'₂ 5aq—ZnA'₂ 2aq four sided prisms—MeA' Oil Formed also from o amido mesitylenic acid

p-Oxy mesitylenic acid $C_2H_2Me_2(OH)CO_2H$ [5 3 4 1] [223°] from p-sulphamido mesitylenic acid by potashfusion (Jacobsen, B 12, 606, A 206, 197) Formed also from p amido mesitylenic acid (Emerson, Am 8, 268) Needles, insol cold Yields c-xylenol on heating with HClAq at 200° —BaA'₂ —AgA' —MeA' [130°] —EtA'

8°] Needles or prisms, volatile with steam OXY-METHACRYLIC ACID Appears to be Appears to be a product of the action of KCy followed by potash on CH₂ CCl.CH₂Cl (Claus, A 170, 126)

Methyl derivative CH₂ C(CH₂OMe) CO₂H (c 238°) Formed by heating C(OMe)₂(CO₂H)₂ at 140° (Kleber, A 246, 103) Liquid, missible with water With HI and P it yields MeI and isobutyric acid

OXY-METHANE v METHYL ALCOHOL Di-oxy-methane v. Formic Aldehyde Tri-oxy methane v Formic ACID OXY-METHANE SULPHONIC ACID CH₂(OH)SO₃H. Formed from methyl alcohol, H.SO., and SO. (Max Müller, B. 6, 1031) Crys-

talline, not decomposed by boiling water or acids. Yields sodium sulphide on warming with soda

and spongy platinum (Loew, B 23, 8125)
Oxy methane disulphonic acid CH,SO, 1.6 OH(OH)(SO,H). Formed from methyl alcohol and SO, ... K,A" needles

Oxy-methane tri sulphonic acid C(OH)(SO₂H)₂. Formed from C(SH)(SO₃K)₂ and bromme-water (Albrecht, A 161, 129) Delquescent mass —K_AM" aq needles S 1 2 at 21° – (NH₄)₂M" —Ba₃M"₂ 8aq —Hg₆O₂A"'₂ 15aq —PbK₁₈A"'₆(OH) 5aq —Pb₄A"'₄Ac; 8aq —Ag₃A''' aq needles, v sol warm vater

OXY - METHENYL - DI - AMIDO-DIBENZOIC

ACID Ethylderivative

C(OEt) NH C.H. CO.H [223°] Formed from o amido-benzoic acid hydrochloride and NH C(OEt)₂ (Sandmeyer, B 19, 2656) Needles, sl sol hot water —AgHA" white proxy METHENYL-AMIDO PHENOL

[1379] Formed by heating oxy-phenyl urea made by the action of ClCO₂Et on o amido phenol (Gronvick, Bl [2] 25, 177, Kalckhoff, B 16, 1828), and by heating o amido-phenyl ethyl carbonate (Bender, B 19, 2265, 2950) Plates EtI and KOEt form C,H,<NEt $[29^{\circ}]$

derivative C.H. COSCOEt Ethyl(225°-230°) Formed from C_sH₄(OH) NH₃Cl and NH C(OEt)₂ (Sandmeyer, B 19, 2655) Oil, ınsol alkalıs

OXYMETHENYL AMIDO PHENYL MER $C_6H_4 < N > C(OH)$ CAPTAN C.H.NOS 1e

Formed by the action of hot water or alcohol on C,H4CISN which is got by heating phenyl thiocarbimide with PCl, (Hofmann, B 12, 1128, 13, 10) Crystals (from alcohol), sl sol water

Ethyl derivative C.H.NS(COEt) From C,H,ClSN and NaOEt -B',H,PtCl,

Acetyl derivative C.H. NS(COAc) DIHÝDŘIDĚ OXY ŤETRAMETHENYĽ CARBOXYLIC ACID CH₂ CH CO₂H CH₂ CO [183°]

Formed by heating inactive amido glutaric acid (Wolff, A 260, 125) Prisms, v sol hot water OXY-METHENYL-PHENYLENE-DIAMINE

PHENYLENE UREA.

OXY - METHYL - ACETOACETIC

Ethyl derivative

CH₂(OEt) CO CHMe CO Et (190°-195°) S G 22 976 Formed from chloro-methyl acetoacetic

ether and NaOEt (Isbert, A 234, 194) Liquid

© OXY-METHYL AMIDO BENZOIC ACID

C₆H₄(CH₂OH)(NH₂) CO₂H [2 4 1] Formed by
dissolving amido phthalide [1789] in hot aqueous potash (Hœnig, B 18, 8452) — CuA', dark grey

Oxy-dimethylamido-benzoic acid Anhy-dride of the methylo-hydroxide CieHisNOs Oxy-dimethylamido-benzoic acid s.e. $C_sH_s(OH) < \frac{NMe_s}{CO} > O$ Formed by the action of MeI and KOH on amido-salicylic acid (Griess, B 12, 2307) White needles (containing 4aq),
▼ sol water Tastes bitter Gives a violet colour with FeCl. Converted on heating into orystalline C_eH₃(@H)(NMe₂)CO₂Me —B'HCL-

B'HI —B',H,PtCl, 4aq small yellow prisms
Ozy-methylamido-benzoic acid Met
dervative C,H,(OMe)(NHMe)CO,H [at Methyl above 200°] Formed from potassium amido anisate and MeI (Griess, B 5, 1042, 6, 588) Slender ncedles, v sl sol hot water Yields B'HClAq Further treatment with MeI and KOH forms C₆H₃<NMe₃>0 5aq which gives the salts B'2H2PtCl6 and B'HI aq, and on distillation yields C,H,(NMe)(OMe)CO,H (288°)

β OXY METHYL a AMIDO BUTYRIC ACID CHMe(OH) CH(NHMe) CO₂H S 56 at 12° Formed from \$\beta\$ methyl glycidic acid and methylamine at 100° (Selinsky, Bl [2] 43, 247)

o OXY-TETRA-METHYL-DI-p-AMIDO-TRI-

PHENYL CARBINOL C2H26N,O2 1 e C6H4(OH) C(OH)(C6H4NMe2), Formed by oxidising the leuco- base obtained by condensation of salicylic aldehyde with dimethylaniline (O

Fischer, B 14, 2522) Dyes yellowish green O OXY-TETRA-METHYL DI p AMIDO TRI-

PHENYL METHANE C2H-N2O1e C.H.(OH) CH(C6H,NMe.). Leuco base of salrcyl allehyde green [128°] Prepared by heating a mixture of dimethylaniline (24 pts), salicylic aldehyde (10 pts), and ZnCl₂ (20 pts) to 100° for 7 or 8 hours, the yield being nearly theoretical (Fischer, B 14, 2522) Colourless rosettes Sol hot alcohol and benzene, nearly insol water Combines with both acids and bases On gentle oxidation it gives a green of yellow shade

Acetyl derivative CzH25N (OAc) Irides

[144°] cent plates

The isomeride [163°] from p oxybenzoic alde hyde yields a green dye and forms an acetyl derivative [146°] crystallising in prisms

Di-oxy tetra methyl di amido tri phenyl methane Methyl derivative C_bH₃(OH)(OMe) CH(C₆H₄NMe) [136°] Formed

from vanıllın, PhNMe, and ZnCl. (O Fischer a Schmidt, B 17, 1895) Crystals, v sol alcohol OXY TETRA METHYL-AMMONIUM HY

DROXIDE CH2(OH) NMe2OH Formed from CH I NMe, I and moist Ag O (Hofmann, J 1859, 377) Yields (CH2OH NMe3Cl)2PtCl, crystallising in octahedra

DI OXY METHYL AMYL KETONE methyl derivative CH(OMe), CO CHEt (134°) SG 15 886 Formed as one of the products of the action of NaOMe upon CHCl₂ CO CEt₂ CO₂Et (James, A 231, 243, C J 49, 57) Oil Miscible with alcohol and with ether, burns with pale flame Does not combine with NaHSO, or react with Ac O

OXY-METHYL AMYL PYRROLE CARB OXYLIC ETHER C.H. NO CMe OC CO.Et [52°]

(188° at 16 mm) Formed from acetosuccinic ether, amylamine, and alcohol in the cold (Emery, A 260, 150) White plates (from CS,)

DIOXY DI METHYL ANILINE v TETRA METHYL DI AMIDO DI PHENYL DI-OXIDE

OXY METHYL ANTHRANOL Acetyl de- $\label{eq:continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous_continuous$ [217°] Formed from methyl anthraquinone [177°] Ac.O, NaOAc, and zing-dust (Lieharmann, B 21, 1172) Plates

OXY METHYL-ANTHRAQUINONE C,5H,0O, $C_eH_4 < \frac{CO}{CO} > C_eH_2Me(OH)$

Formed by heating o cresol phthalein or a mixture of phthalic anhydride, o cresol, and H2SO, at 160° (Baeyer a Fraude, B 12, 241, A 202, 163) Yellow leaflets

Bromo - derivative [205°] Oxy methyl-anthraquinone

C₆H₄ C₂O₂ C₆H₂Me(OH) [1625][170°] Formed in like manner from p cresol (Drewson, A 212, 346, Birukoff, B 20, 2069) Orange needles (by sublimation)

Acetyl derivative [180°] Needles Oxy methyl anthraquinone C₁₄H₆MeO₂(OH) 8°] Formed from amido methyl anthraquinone [202°] by the diazo reaction (Römer a Link, B 16, 699) Yellow needles (by sublima tion)

Acetyl derivative [177°] Plates

Di oxy methyl anthraquinone $C_6H_3(OH) C O_2 C_6H_2Me(OH)$ [162°] Mol w The 254 S (boiling 86 pc alcohol) 45 yellow colouring matter of rhubarb, the wall lichen (Parmelia parietina), and of the root of Rumex obtustfolius (Rochleder a Heldt, A 48, 12, Döpping a Schlossberger, A 50,215, De la Rue a Muller, C J 10, 298, Thann, A 107, 324) It occurs also in the root of Rheum pyramidale, Rumex palustris, and of other varieties of Rumex (Grothe, P 113, 190) and in senna leaves (Batka, C C 1864, 622) Formed by passing air through an alkaline solution of chrysarobin (Liebermann a Seidler, A 212, 36) Golden plates (from alcohol), forming a cherry red solution in NaOHAq Insol Na.CO₄Aq Cone HSO₄ forms a red solution Cone HNO₃ forms a tetra nitro derivative Yields methyl anthracene on distilling with zinc dust Does not dye mordants Zinc, HOAc, and HClAq form C15H12O3 [200°-206°] whence C₃₀H₂₀Ac₆O, [231°] (Liebermann, B 21,

Di acetyl derivative [200°] Di benzoul derivative [c 201°]

Di oxy methyl anthraquinone C₆H, C₂O C₆HMe(OH)₂ [16325] Methyl-quinizarin [160°] Formed from hydrotolu Methylquinone, phthalic anhydride, and H SO, at 140° (Nietzki, B 10, 2011) Red needles (from alcohol) Yields methyl-anthracene when distilled with zınc dust

Acetyl derivative [185°] Needles

Di oxy methyl anthraquinone $C_6H_4C_2O_2C_8HMe(OH)_2$ [1 6 4 3 2] Methul-Formed by potash fusion alizarin [252°] from bromo or oxy methyl anthraquinone (O Fischer, B 8, 675, Fraude, B 12, 241) Orange needles, which may be sublimed Dyes mordants lıke alızarın

Alkannin (vol 1 p 125) is probably a di oxymethyl - anthraquinone as it yields methylanthracene on distillation with zinc dust (Liebermann a Römer, B 20, 2428)

D1-oxy-d1-methyl-anthraquinone C.H.Me(OH) C.O. C.H.Me(OH) Di - methyl-anthrarufin [300°] Got, together with the two following isomerides, by the action of H2SO4 on s-oxy-toluic acid (Kostanecki a Niementowski, B 18, 255, 2140, A 240, 276) Yellow needles (from benzene) Its alkalıne solutions are yellow Does not dye mordants

Di acetyl derivative [237°] Tables Di oxy-di-methyl-anthraquinone

C_{1.}H_.Me₂(OH)₂O₂ D1-methyl-anthraflavic acid Needles or small yellow plates (by sublimation), not solid at 360° Does not dye mordants

Dr-acetyl derivative [223°] Needles Dr-oxy-di-methyl anthraquinone (benz) [213°]. Yellow needles, yielding C₁₆H₁₆Ac₂O₄ [188°]

Tri-oxy-methyl-anthraquinene $C_{13}H_{10}O_3$ Emodin [254°] Occurs in rhubarb root (Warren de la Rue a Hugo Müller, C J 10, 304), in the bark and berries of Rhamnus frangula (Liebermann a Waldstein, B 8, 970, 9, 1775, Schwabe, Ar Ph [3] 26, 569), and in the lichen Nephroma Lusitanica (Bachmann, C C 1888, 47) Orange red monoclinic prisms (containing aq) Yields methyl anthracene on distilling with zinc dust. Its alkaline solution is dark cherry red

Mono-acetyl derivative [180°] Tri-acetyl derivative [190°]

Tri oxy methyl anthraquinone

[*_4H_Me C,O_2 C_4H(OH)_* [1 6 2 3 4] Methylanthragallol [c 375°] Made by heating gallic
acid with p toluic acid at 130° for 15 hours
(Cahn, B 19, 2335, A 240, 284) Orange red
needles (by sublimation) Its solution in cone
KOHAq is green, becoming violet on dilution
Hot NH₄Aq forms a blue solution Cone H₂SO₄
forms a red liquid turned green by a trace of
HNO₃, decolourised by more HNO₃

Tri-acetyl derivative [204°]
Tri oxy methyl anthraquinone

[2' 1' 6'] C₆H₃Me C₂O₂ C₆H(OH)₃ [1 6 2 3 4] Methyl anthragallol [298°] Formed by heat ing gallie acid with o toluic acid (C) Minute yellow needles Forms a green solution in conc KOHAq turned violet on dilution Dyes like anthragallol Conc H₂SO₄ gives a red solution turned green by HNO₃

Tri-acetyl derivative [210°] Tables (2, 3, 4) Tri oxy 3' and 5' methyl anthra quinones (methyl anthragallols) These two isomerides are formed simultaneously by heating gallic acid with m toluic acid at 130°-135°. The one melts at [612°] and gives an acetyl derivative which forms needles melting at [190°] The other isomeride melts at [235°-240°], and its acetyl derivative, which crystallises in small prisms, melts at 218° Their other properties are almost the same as those of the other methylanthragallols (Cahn, B 19, 2336)

Tri-oxy-methyl anthraquinone

[3 2 1 6] C₆H₂(OH), C₁O₂C₆H₂Me(OH) [1' 6' 2' 5'] Methyl-oxy alızarın Formed by saponifying its di-methyl ether which is produced by heating hemipic acid with p cresol and H₂SO₄ (Lieber mann a Kostanecki, A 240, 303) Brownish-yellow flakes, v sol alcohol Dyes like alızarın

Dr-methyl ether C17H14O5 Flakes Tri-oxy-di-methyl-anthraquinone

[4'2'1'6'] C₀H₂Me₂ C₂O₂ CH(OH), [1 6 2 3 4] Formed by heating (4,2,1)-di methyl benzoic acid with gallic acid and H₂SO₄ (Birukoff, B 20, 871, A 240, 287) Yellowish-red needles Forms a red solution in cone H₂SO₄ Yields dimethyl anthracene [224°], when distilled with sinc-dust

Tri-oxy-tri-methyl-anthraquinone

[4' 3' 2' 1' 6'] C, HMe, C, O, C, H(OH), [1 6 2 3 4]

Trn-methyl anthragallol [244°] Formed from tri methyl benzoic (durylic) acid, gallic acid, and H,SO, (Wende, B 20, 867) Brown seedles Yields tri methyl anthracene [236°]

Acetyl derivative [174] Plates Tetra-oxy-di-methyl-anthraquinone [2' 4' 5' 1' 6'] C₆HMe(OH), C₁O₂ C₆HMe(OH)₄ [1 6 2 3 4] Di methyl anthrachrysone [above

[1 6 2 3 4] Den methyl anthrachrysone [above 360°] Formed by heating di oxy-o toluic acid with H₂SO₄ (10 pts) at 100° (Cahn, B 19, 755) Reddish yellow plates (by sublimation) Does not dye mordants

Tetra acetyl derivative [234°]
OXY-METHYL-BENZOIC ACID v Oxy
TOLUIC ACID

Oxy di methyl benzoic acid

 $C_0H_2Me_2(OH)$ CO.H [6 3 2 1] Oxy isoxylylic acid [142°] Formed by fusing ethyl p xylene sulphonic acid with potash (Stahl, B 23, 991) Needles Gives a bluish violet colour with FeCl₂

Oxy-di methyl benzoic acid

C₆H_{*}Me₂(OH) CO_.H[5 4 2 1] Oxy p xylylve acid [199°] Formed from ψ cumenol by potash fusion (Reuter, B 11, 30, Jacobsen, B 12, 436) Needles, volatile with steam Gives a bluish violet colour with FeCl₃ HClAq at 220° gives xylenol [61°]—BaA'₂ S 1 1 at 0°

Oxy di methyl-benzoic acid C₀H₂Me₂(OH)CO₂H [4 2 5 1] ? [170 5°] Formed by fusing C₀H Me.BrCO H (Gunter, B 17, 1608) Scarcely volatile with steam Gives no colour

with FeCl.

Oxy di methyl benzoic acid [137°] Formed from p xylenol, Na, and CO, at 180° (Oliveri, G 12, 166) Needles, coloured violet by FeCl₃ — BaA'₂ 4aq

Oxy-di methyl benzoic acid

C₆H Me₂(OH)CO H [6 3 4 1] [153°] Got from C₆H Me₂Br CO H and KOH Not coloured blue by FeCl₃

Oxy di methyl benzoic acid Xyletic acid [155°] Formed from crude xylenol, Na, and CO (Wroblewsky, Z 1868, 233) —CaA', 2aq —BaA', 2aq needles

Di oxy di methyl-benzoic acid

C_sHMe_s(ŎH),CO_sH [5 3 6 2 1] [196°] Formed from betorein, NaHCO_s, and water at 130° (Kostanecki, B 19, 2323) Prisms Coloured blue by FeCl_s

Oxy tri-methyl-benzoic acid

C_aHMe₄(OH)CO₂H [6 4 3 2 1] Oxydurylic acid [148°] Formed by fusing durenol with potash (Jacobsen a Schnapauff, B 18, 2844) Needles

—CaA'₂ aq prisms, m sol water

Di oxy-tetra methyl benzoic acid Tetra
hydride of the methylene derivative
CH₂O₂H₄Me₄CO₂H Piperhydronic acid [96°]
Formed from (β)-hydropiperic acid and sodium
amalgam (Buri, A 216, 178) —CaA'₂ aq orystals
(from water)

OXY TRI-METHYL-BENZOIC ALDEHYDE C₈HMe₂(OH)CHO [1 3 4 6 5] [106°] Formed by the action of chloroform on an alkaline solution of \(\psi\$ cumenol (Auwers, B 17, 2976) Needles FeCl₂ gives a blue colour OXY-METHYL-BUTYL-PYRROLE CARB-

OXY-METHYL-BUTYL-PYRROLE CARB-OXYLIO ETHER C,H, N < CO .CH, [68°]. (175° at 15 mm) Formed from aceto succinic ether (10g) and isobutylamine (34g) in the cold (Emery, A 360, 149) Needles (from CS₂) OXY METHYL CINNAMIC ACID Anhy-

dride 6 4 \frac{1}{2} \cap C_6 H_2 Me(OH) < \frac{CH CH}{O-CO} [248°] H-moumbelliferon Formed by heating orein with malic acid and H_SO_4 (Pechmann a Welsh, B 17, 1649) Tables, sol alcohol and aqueous alkalis Conc H SO_4 forms a solution with blue fluorescence Potash fusion gives orcyl alde hyde and KOAc

Acetyl derivative [127°] Formed by heating orcyl aldehyde with Ao,O and NaOAc (Tiemann a Helkenberg, B 12, 1002) Needles OXY METHYL COUMARILIC ACID CieHsO4

Formed by saponification of its ethyl ether, which is obtained by boiling chloro acetacetic ether (1 mol) with a cone alcoholic solution of mono sodium resorcin $C_sH_s(OH)(ONa)$ Needles (containing $\frac{1}{2}aq$) V sol hot water On distillation it loses carbonic acid, giving oxy methyl counarone $C_sH_s(OH)(CNa)$ (197°)

Ethylether A'Et [178°], white needles, v sol ether, its dilute solutions have a blue fluorescence (Hantzsch, B 19, 2928)

D1-oxy-methyl-coumarilic acid $C_{10}H_4O_3$ i.e. $\begin{bmatrix} 6 & 4 & 2 \\ 1 & 2 \end{bmatrix} C_8H_4(OH)_2 & \bigcirc CODH & [281°] \end{bmatrix}$ Formed by saponification of its ethyl ether, which is obtained by boiling chloro acetacetic ether (1 mol) with a cone alcoholic solution of mono sodium phloroglucin $C_4H_4(OH)$ (ONa) (1 mol) C_{10} -tals (containing $\frac{1}{2}$ aq) The acid and its ether give an indigo blue colour with warm cone $H SO_4$

Ethyl ether A'Et [242°], small white needles, the alkaline solution is fluorescent (Lang, B 19, 2934)

OXY METHYL COUMARONE v COUMARONE OXYMETHYLENE v FORMIC AIDEHYDE OXY-TRIMETHYLENE-DIAMINE

CH(OH)(CH₂NH₂). Formed by heating with HClAq the compound got by the action of epichlorhydin or (a) dichlorhydin on potassium phthalimide (Goedeckemeyer, B 21, 2689, Gabriel, B 22, 225)—B"H₂Cl₂ [184°] Hygro scopic mass—B"H PtCl₄ [240°]—B"H₂Br₂ [200°] Needles—B"2C₈H₂(NO₂)₃OH yellow needles [230°]

OXY TRIMETHYLENE DIPHTHALAMIC
ACID CH(OH)(CH,NH COC,H,CO,H), [c
120°] Formed by boiling oxytrimethylene
diphthalimide with potash (Goedeckemeyer, B
21, 2690) Hygroscopic needles Yields oxytrimethylene diamine on evaporating with
HClAq

OXYMETHYLENE-PHTHALIDE? C₆H₆O₃ [146° A crystalline body formed in the action of Br and HOAc on acetophenone carboxylic acid (Gabriel a Michael, B 11, 1010)

Phenyl derivative C,H, COO

[144°] Made by heating phthshic anhydride with phenoxy acetic acid and NaOAc (Gabriel, B 14, 922) Needles The homologous p-tolyldervvative [174°] is also crystalline

OXYTRIMETHYLENE - DIPHTHALIMIDE CH(OH)(CH₂NC₈H₄O₂)₂ [205°] Formed from potassuum phthalumide and (a)-duchlorhydrin at 150° (Goedeckemeyer, B 21, 2689, Gabriel, B 22, 224) Needles (from HOAc) Fuming HBr at 200° converts it into CHBr(CH₂NH₂)₂

OXY-METHYL-ETHYL-BENZOIC AGID C_sH₂MeEt(OH) CO₂H [149°] Made by fusing s di methyl ethyl benzene sulphonic acid with potash (Jacobsen, A 195, 284) Long needles from dilute alcohol) Turned blue by FeCl,

OXY METHYL-ETHYL KETONE Ethyl dervative CH₂(OE) CO Et (100°-105°) (Formed from CH₂(OE) CO CHMe CO₂Et and alcoholic KOH at 120° (Isbert, A 234, 196)

OXY - METHYL - ETHYL - PYRIMIDINE $C_1H_{10}N_2O$ is $CEt < N COH \\ N COH \\ COH > CH$ [160°] Formed by the action of a 10 pc solution of NaOH (1 mol) upon a mixture of propionamidine hydrochloride (1 mol) and acetacetic ether (1 mol) (Pinner, B 18, 2847, B 22, 1619) Fine white needles V sol water and alcohol Reduced by zinc dust to methyl ethyl pyrimidine

Salts -B'HCl [240°-246°], very soluble thick prisms - B'₂H₂Cl₂PtCl₄ [236°], thick yellow prisms

Oxy methyl di ethyl pyrimidine

CEt N CMe CEt [135°] Formed from propnonamidine hydrochloride, ethyl acetoacetic ether, and dilute (10 pc) NaOHAq (Pinner, B 22, 1621) Needles, v sol water

oxy methyl di ethyl pyrimidine C₂H₁₄N₂O

i.e. CEt N C(OH) CMe [155°] Formed
from propionamidine hydrochloride, propionyl
propionic ether, and KOH (Meyer, J pr. [2] 39,
264) When warmed with a solution of introus
acid in HOAc it yields C₂H₁, N₄O₂ and a little
C₂H₁, N₄O₂ [265°]

Oxy di methyl ethyl pyrimidine

 $CMe \stackrel{N}{\sim} NCMe \longrightarrow CEt$ [146°] Formed from acetamidine and ethyl acetoacetic ether (Pinner, B 22, 1618) Needles, v sol water

Oxy di methyl-ethyl pyrimidine

Oxy di methyl-ethyl pyrimidine $CMe < N CEt \over N C(OH) > CMe$ [168°] Formed from acetamidine and propionyl propionic ether (E von Meyer, J pr [2] 40, 304)

D1-oxy-methyl-ethyl-pyrimidine
C4H.MeEt(OH),N2 1.6 CO NH CMe
NEt CO

Methyl cthyl uracil [195°] Formed, together with di-oxy methyl di ethyl pyrimidine [58°], by heating potassium methyl uracil with EtBr at 155° (Hoffmann, A 253, 68) Prisms (from EtBr) or needles (from alcohol)

OXY-METHYL-ETHYL-PYRROLE CARB

OXY-METHYL-ETHYL-PYRROLE CARB OXYLIC ETHER Net CMe CO.Et [76°] (165° at 14 mm) Formed from acetyl-succinio

ether and cold aqueous ethylamine (Emery, A 260, 148) Needles

Oxy-methyl-ethyl-pyrrole dihydride carboxylic acid CO NEt CMe CO₂H [123°] Obtained, as nitrile, by heating acetyl propionic (levulic) ether with HCy and alcoholic ethyl amine (Kühling, B 23, 709) Needles, v sol water and alcohol

Netrile $0.H_1, N_2O$ Syrup Amide $0.H_1, N_2O$ [183°] Needles Throamide [176°] Formed from the nitrile

and alcoholic H₂S

Amidoxim [c 160°] Formed from the thioamide by boiling with hydroxylamine hydro

OXY- $(B \ 2 \ Py \ 2)$ -DI-METHYL - $(Py \ 3)$ -ETHYL QUINOLÎNE C₁₃H₁₄(OH)N [45°] (312°-316° at 720 mm) Colourless crystals Formed by fusing di-methyl ethyl quinoline sulphonic acid with KOH —A'K' easily soluble colourless plates (Harz, B 18, 3390)

Di-oxy-methyl ethyl quinoline

 $C_6H_3Me < N = COH$ [c 220°] Formed from chloro ethyl oxy o toluquinoline and dilute HCl at 165° (Rugheimer a Schramm, B 20, 1235, 21, 302) Needles (from HOAc), insol water

Reference - CHLORO OXY METHYL ETHYL. QUINOLINE

α-OXY-α-METHYL GLUTARIC ACID

ie CO₂H CMe(OH) CH₂.CH₂ CO₂H C.H.O. Formed from the lactone of oxy isohexoic acid by oxidation with dilute nitric acid (Fittig a Bredt, A 208, 63, 236, 225) Made also by saponification of the nitrile formed by combination of β acetylpropionic (levulic) acid with HCy (Kreckeler a Tollens, B 18, 2018, A 238, 287) The free The free acid at once changes to the lactonic acid BaA" 4aq — SrA" 4aq — CaA" 7aq — ZnA" — Ag2A" white flocculent pp

Lactonic acid CMe(CO₂H) < CH₂ CH₂ CO₂ Deliquescent prisms, v sol ether Converted by hot H₂SO₄ into CO₂ and levulic acid CaA'₂4¹2aq —MeA' (252°) —EtA' (262°)

Amide of the lactonic acid [c 124°] Nitrile of the lactonic acid [c 33°]

 β -Oxy β methyl-glutaric acid

Ag₂A".

acid CMe₂ CH₂ CMe CO₂H ? [104°] Oxy-tri methyl glutaric acid Lactonic Formed

from a bromo tri methyl glutaric anhydride and KOHAq at 0° (Auwers a V Meyer, B 23, 307) Crystals, v sol water — AgA' crystalline powder

D1-oxy-di-methyl glutaric acid? $CH_2(CMe(OH) CO_2H)_2$? [96°] Formed by dissolving di a bromo-di a methyl glutaric anhydride in cold 10 pc caustic soda solution (Auwers a. Jackson, B 23, 1614) Six sided plates, v sol cold water

OXY-METHYL-INDONAPHTHENE

 $C_0H_2M_0 < CH_2 > CH$ [59°] Formed by condensing m tolyl propionic acid by means of hot H₂SO₄ (Von Miller, B 23, 1899) White needles with characteristic odour Volatile with steam

The isomeride from p tolyl propionic acid melts **at** 63°

Oxy methyl-indonaphthene

 $C_0H_4 < C_{C(OH)} > CMe$ $(246^{\circ}$ at 719 mm). Formed from β phenyl isobutyric acid and H2SO, at 150° (Von Miller, B 23, 1888) Heavy oil smelling of peppermint, volatile with steam Yields phthalic acid on oxidation phenyl hydrazide [116°]

OXY METHYL INDOLE Ethyl deriva

tve $C_{\mathfrak{o}}H_{\mathfrak{s}} < \stackrel{NH}{\underset{C(\mathrm{OEt})}{}} > CMe \ \text{or} \ C_{\mathfrak{o}}H_{\mathfrak{s}} < \stackrel{NH}{\underset{CH}{}} > C \ \text{CH,OEt}$ [142°] Formed by heating at 90° the phenylhydrazide of CH, CO CH, OEt (Fittig, B 21, 2649) Crystals (from alcohol)
OXY-METHYL-JULOLE DIHYDRIDE

 $\begin{array}{c} \mathrm{CH} < \mathrm{CH} < \mathrm{CH} < \mathrm{CH} < \mathrm{CH} < \mathrm{CH} > \mathrm{C} < \mathrm{CMe} > \mathrm{CH} \\ \mathrm{CH} < \mathrm{CH} < \mathrm{CH} < \mathrm{CH} > \mathrm{C} < \mathrm{CMe} > \mathrm{CH} \\ \end{array}$ [130° cor]

Formed by boiling quinoline tetrahydride with acetoacetic ether (Reissert, B 24, 845) White needles, v sol alcohol, insol alkalis, sol conc HClAq - B'HCl 11aq - B'2H,PtCl orange

OXY METHYL MALONAMIC ACID

C4H7NO4 2 e CMe(OH)(CONH2)(CO2H) Formed from pyruvic acid and KCy followed by conc HClAq (Bottinger, B 14, 88) Syrup -, xaq crystalline, v e sol water

DI OXY DI METHYL MALONIC ACID Di methyl derivative (CH₃O CH₂),C(CO H) [138°] Formed from sodium malonic ether, chloro di methyl oxide and NaOEt (Klebei, A 246, 111) Prisms, v sol water Its salts are very hygroscopic

Diethylether C,H10O2(CO2Et)2 (c 240°) OXY-DI-METHYL PENTAMÉTHENYL

HYDRIDE COCCH, CMe or

co< 'Dr methyl ketopentene' (119°) Made from methyluvic acid by pro longed boiling (Dietzel, A 250, 195) lighter than water

Oxy methyl heptamethenyl trihydride?

C₈H₁₂O i e CH CMe CH₂ CH₂ CH₂ (189°) oil, smelling like camphor, formed by heating its dicarboxylic ether which is formed by distilling CO_Et CHAc CH₂ CH₂ CHAc CO₂Et (Perkin a Obrembsky, B 19, 2051) Reacts with

phenyl hydrazine DI-OXY-DI-METHYL-HEPTAMETHYLENE (201°

at 180 mm) Formed by reducing $\mathrm{CH}_2(\mathrm{CH}_2\mathrm{CH}_2\mathrm{Ac})_2$ with sodium (Kipping a W H Perkin, jun, C J 59, 220) Thick oil with burning taste, smelling of thyme Does not form an oxim or a phenyl hydrazide Yields deliquescent C₂H₁₇NaO, aq Forms an oily product of condensation C₁₈H₂₄O₃ (305°-310° at 200 mm)

Dr-acetyl derivative C, H, Ac, O, (201° at 65 mm) Liquid, insol cold water

OXY METHYL-(a)-NAPHTHOQUINOLINE $C_{14}H_{11}NO$ is $C_{10}H_{4} < N = C_{Me} [292^{\circ}]$ (K), [over 300°] (C a L) Formed by boiling with HCl a naphthyl β imido-butyric ether, which is formed by condensation of acetoacetic ether with (a)-naphthylamine (Knorr, B 17, 543, Conrad a. Limpach, B 21, 531) Needles (from alcohol) -B'₂H₂PtCl₆ v sl sol hot water

The isomeride derived from (3) naphthylanaine crystallises in flat needles [286°] (K.) or [above 300°] (C a L) decomposed by distilla

OXY-DI-METHYL (β)-NAPHTHOQUINOL-INE DISULPHONIC ACÍD

C₁₅H₁₁(OH)(SO₅H)N 1½aq Formed by potash fusion from the disulphonic acid of di methyl-(8) naphthoquinoline (Reed, J pr [2] 35, 309) small needles, insol water and alcohol

DI-OXY-METHYL-NAPHTHOQUINONE (?) [170°] Extracted from tubers of Drosera Whittakeri (Rennie, C J 51, 376) Forms a deep red solution in KOHAq

Tri oxy methyl-naphthoquinone (?) C11H8O5 [c 193°] A substance of this empirical composition may be extracted from tubers of Drosera Whittakeri (Rennie, C J 51, 371) Red plates (from alcohol or glacial HOAc) V si plates (from alcohol or glacial HOAc) sol water Gives a violet solution in KOHAq or NH_sAq Reduced by SnCl₂ to C₁₁H₁₀O₅ [217°

OXY-METHYL-ISO OXAZOLE

 $CMe \leqslant_{N-O}^{CH_2} \stackrel{CO}{O}$ [170°] Formed from acetoacetic ether, hydroxylamine hydrochloride, and NaOH at 50° (Hantzsch, B 24, 497) needles, sl sol cold water, sol HClAq -Ac O forms on heating a compound [136°] possibly N = 0 C C C CMe N NH A' [207°] = N - O C C C C (OAe) O -NH₄A' [207°] -BaA' 2aq -CuA' -AgA gelatinous

Di oxy di methyl di iso oxazyl $^{0.CO}_{N.CMe}$ CH CH $<^{CO.O}_{CMe.N}$ Formed by warm ing isocarbopyrotritaric ether with hydroxylamine and HOAc on the water bath (knorr, B 22, 161) Han like needles which explode at 190

OXY-TETRA-METHYL-PHENYL ACETIC ACID [6 5 3 2 1] C, HMe, CH(OH) CO H [146°] Formed from tetra methyl phenyl glyoxylic acid by reduction with sodium amalgam (Claus a Foecking, B 20, 3102) Nodules -BaA'2 2aq -CaA', 8aq needles

Oxy tetra-methyl-phenyl acetic acid [6 5 4 3 1] C₆HMe₄ CH(OH) CO₂H [160°] Formed in like manner (Claus, J pr [2] 38, 283) Hexahedra, m sol hot water

Oxy tetra methyl phenyl acetic acid [6 4 3 2 1] C₆HMe, CH(OH) CO₂H [156°] Prisms, v sol alcohol and ether -NaA' 12aq -

CaA' 8aq —BaA' 3aq small crystals
OXY-TRI - METHYL - PHENYL METHYL-

PYRAZOLE C₁₂H₁₆N₂O t c
C₆H₂Me₂ N < CO CH₂
N=CMe
 [15] [155°] Formed by heating the \(\psi \) cumyl hydrazide of acetoacetic ether at 140° for two hours (Haller, B 18, 706) Glistening crystals, v sol alcohol Yields a nitrosamine C₁₂H₁₅N₂O₂[156°] and a methyl derivative C₁₄H₁₈N₂O [106°]
OXY - TETRA - METHYL - PHENYL - DI -

METHYL-PYRIDINE CARBOXYLIC ACID $C_{e}HMe_{4}N < CMe C(CO_{2}H) > [145°]$ Made by

heating tetramethyl phenyl amido crotonic ether at 280° (Conrad a Limpach, B 21, 1655) OXY-METHYL-ISOPHTHALIC ACID

 $C_sH_sMe(OH)(CO_2H)_2$ [4 5 3 1] [c 270°] Formed by heating $C_sH_sMe(SO_sH)(CO_2H)_2$ with cone HClAq at 220° (Jacobsen, B 14, 2115) Needles (from hot water) Not coloured by FeCl

OXY-DI-METHYL-PROPIONAMIDINE CH, CH(OH) C(NHMe) NMe The crystalline hydrochloride B'HCl [215°], formed by the action of methylamine on the hydrochloride of CH₃ CH_(OH) C(OC₅H₁₁) NH, is v sol water and m sol alcohol (Pinner, B 23, 2948)

OXY-METHYL-PROPYL-BENZÓIC Methyl derivative CeH2MePr(OMe)CO.H [3 6 1 4] [139°] Formed from its amide [149°], which is made by the action of ClCONH₂ on C.H.MePr(OMe) in CS, in presence of AlCl. (Gattermann, A 244, 68) The ethyl derivative [159°] and its amide C.H.MePr(OEt) CONH. [127°] are got in like manner

Oxy-methyl isopropyl-benzoic acid

U₆H₂MePr(OH)CO₂H[3 5 2 1] Cymenotic acid [147°] Formed from (4,2,1) cymenol, sodium, and CO_2 (Jesurun, B 19, 1414) and $ext{CO}_2$ (Jesurun, B 19, 1414) Slender needles (from water) — BaA'_24aq — AgA' — MeA' [148°] Isomeric acids v Carvacrotic acid and

THYMOTIC ACID

OXY-METHYL-PROPYL-CINNAMIC [1 4 3 6] C₆H₂(CH₃)(C₃H)(OH) C₄H₂ CO.H Thymo acrylic acid [280°] Prepaied by heat

ing p thymotic aldehyde with acetic anhydride and sodium acetate (Kobek, B 16, 2104) White microscopic crystals

Methyl derivative C_bH (CH_s)(C_sH_7)(OMe) CH_2CO_2H [141°] Needles, v sol alcohol, sl sol water AN

OXY-METHYL PROPYL-CINNAMIC HYDRIDE v METHYL PROPYL COUMARIN

OXY METHYL PROPYL KETONE Ethylether_EtO CH2 CO Pr (112°-115°) Formed from EtO CH_rCO CHEt CO Et and alcoholic KOH at 120° (Isbert, A 234, 195) Lighter than water, smells like a ketone
DI OXY METHYL ISOPROPYL-PYRIMID-

 $CMe_2(OH)\ C{\leqslant}_{N\ C(OH)}^{N\ CMe}{\geqslant}CH$ Formed from oxy-isobutyramidine hydrochloride,

acetoacetic ether, and NaOH in equivalent proportions (Pinner, B 22, 2625) Needles (from acetone), v sol most solvents

OXY METHYL PROPYL PYRROLE CARB. OXYLIC ETHER C₃H,N-CMe CO₂Et [50°]. (172° at 15 mm) Formed from aceto succinio

ether and propylamine in the cold (Emery, A 260, 148) Needles OXY METHYL PURIN C, H, Me(OH)N, s.s.

 $co <_{NMe}^{NH-CCH} \xrightarrow{N} cH$ [233°] heating di chloro oxy methyl purin with HI (Fischer, B 17, 332) Prisms, v sol water Alkaline in reaction—B'HI—B'₂H₂PtCl₅

C_bH₂Me(OMe)N₄? Oxy-di-methyl-purm [112°] Formed from di chloro oxy di methylpurin and HIAq (Fischer, B 17, 334) Slender needles, v sol water, msol alkalıs

Di-oxy-di methyl purin C,H,N,O, Formed by reducing the ethyl derivative of chloro-dioxy di methyl purin with HI Sparingly soluble crystals

Desthyl derivative CoH, N.O. 10 C(OEt) N C(OEt) C NMe CO? [127°] Formed from di-chloro oxy-di methyl purin and alcoholic NaOH Fine plates, sol HClAq, insol alkalıs

Tri-oxy-methyl-purin v METHYL URIO ACID OXY-METHYL-PYRAZOLE C,H,N2O 16 $CMe \leqslant_{N-NH}^{CH_2} CO$ [215°] Formed by warming acetoacetic ether with hydrazine and water (Curtius a Jay, J pr [2] 39, 52) Prisms (from water), sl sol hot alcohol Has a sweet taste OXY-DI-METHYL-PYRIDINE Ethyl de-

rivative C.H.,NO is NCCOEt CHCOMe (246°) Formed from acetoacetic ether and ammonia zinc chloride (Canzoneri a Spica, G 16, 449) Oil

Oxy-di methyl-pyridine Methyl derivatrve N<CMe CH>C OMe. (203°) SG 👯 1011 Formed from chloro-di methyl pyridine, NaOMe, and MeOH at 160° (Conrad a Eck hardt, B 22, 81) Oil -B'zHzPtCla -B'MeI 4°] Prisms (from water)
Ethyl derivative C,H,EtNO

(215°) -B'MeI [196°] Crystals (from water)

Oxy di methyl-pyridine C,H,NO ve

NH CMe CH CMe. \(\psi \) Lutidostyril Formed by heating oxy tri methyl pyridine (methyl \(\psi\) lutidostyril) in a current of HCl (Hantzsch, \(B\) 17, 2904) Formed also by distilling its carboxylic acids (Collie, B 20, 446, Nieme a Pechmann, A 261, 205), and by passing dry NH, over mesitene lactone at 160° (Anschutz, A 259,169) Needles (from alcohol) — B'HCl 2aq prisms — B'₂H₂PtCl₈ — C₇H₈KNO silvery silvery spangles, sl sol KOHAq

Oxy di methyl-pyridine C,H,NO 1.6

CO CH CMe NH Lutidone [231°] (Collie, (350°) Formed by heating its C J 59, 177carboxylic or dicarboxylic acid at 280°, and also by heating dehydracetic acid with NH, at 100° (Haitinger, B 18, 452, Conrad a Guthzeit, B 20, 156) Formed also from di acetyl acetone and NH,Aq (Feist, B 22, 1571) Monoclinic pyramids (containing 3aq) PCl₈ gives chloro-dimethyl-pyridine (178°) FeCl₈ gives a brownish-red colour—B'₂H_PtCl₈ (at 100°) [231° cor]— $B'_{2}H_{2}Or_{2}O, [125^{\circ}] - B'O_{6}H_{2}(OH)(NO_{2}), [220^{\circ}]$

Oxy tri methyl-pyridine C₈H₁₁NO i e CO CH CMe NMe. Methyl-lutidone [245°] Formed by heating its dicarboxylic acid (Conrad a Guthzeit, B 20, 159) Needles (containing Saq)[111°], v sol water —B'HI [242°] Formed by heating lutidone with MeI and MeOH at 140° (Conrad a Eckhardt, B 22, 80) Crystals

Oxy-tri-methyl pyridine C.H., NO 2 e NMe<CMe CH CMe Methyl \psi-lutidostyril (292°)Formed by heating 'dicarbocollidyhum dehydride' with H₂SO₄ or HCl at 150°-180° (Hantzsch, B 17, 1025, 2908) Formed also by methylation of ψ-lutidostyril Very hygroscopic crystals, not volatile with steam. V. sol. water, v. sl. sol. ether.—B'HCl lag —

B',HI - B',H,PtCl,2aq - B',H,PtCl,2EtOH -B'2H,PtCl, long yellowish red needles

Di-oxy-tri-methyl-pyridine Di-ethyl de-rivative N CMe C(OEt) CMe (218°) at (218°) at Formed from di bromo-collidine and

NaOEt (Pfeiffer, B 20, 1850) Oil —B'2H2PtGl6 OXY - DI - METHYL - PYRIDINE CARB -

OXYLIC ACID CMe NH CMe CH—CO C CO2H Lutrdone carboxylic acid [258° cor] Got by saponifying its ether Crystals (containing aq) -BaA'2-CuA'₂ —AgA' [164° cor] amorphous Ethyl ether (240°-250°) Formed in small quantity in distilling & amido crotonic ether under reduced pressure (Collie, A 226, 310, $C \ J \ 59, \ 174)^{-}$ Needles, sol water, sl sol alcohol Does not react with Ac₂O or phenyl hydrazine Yields a bromo derivative $C_{10}H_{12}BrNO_{3}$ [250°] PCl₅ forms $C_{10}H_{12}ClNO_{2}$ (264° cor) which yields a chloro-di methyl-pyridine (177°-180°) on heating

Oxy-di-methyl pyridine carboxylic acid

CO CH CMe CO₂H [258°] Formed from isodehydracetic acid and ammonia (Nieme a Pechmann, A 261, 206)

Oxy methyl-pyridine dicarboxylic acid $oldsymbol{v}$ METHYL CHELIDAMIC ACID, vol 1 p 729

Oxy-di-methyl pyridine dicarboxylic acid CO CH C(CH, CO,H) Ψ Lutidostyril di carboxylic acid [2016] Formed from citra cumalic acid and NH3Aq (N a P) Needles, v sl sol cold water and alcohol

Oxy di-methyl pyridine carboxylic acid

CO CH CMe CO2H Ethyl ether EtA'. **↓** Lutidostyril carboxylic ether [137°] Formed by passing dry NH, through mesitene carboxylic acid lactone at 160° (Anschutz, A 259, 173) It is also a product of the condensation of amido acetoacetic ether and of β amido crotonic ether (Collie, B 20, 445) Needles (from hot water) The corresponding acid is an insoluble crystalline powder [300°]

Oxy-di methyl-pyridine dicarboxylic acid COCCO2H) CMe NH [267°] Made by saponifying its ether Prisms (from water) — KA'—CaA" 2aq —CuA" 1½aq (dried at 100°)

Ethyl ether Et₂A" [221°] S (alcohol) 1

at 20° Formed by adding NH, Aq to an alcoholic solution of $CO < \frac{C(CO_2Et)}{C(CO_2Et)} \frac{CMe}{CMe} > O$ obtained from cupric acetoacetic ether and COCl, (Conrad a Guthzeit, B 19, 24, 20, 154) Forms an acetyl derivative C15H19NO [65°] -B'2H PtCle. [190°] Orange pp

Oxy-tri methyl-pyridine dicarboxylic acid CO C(CO₂H) CMe NMe [245°] Formed by saponitying its ether (C a G)—Na,A" crystalline, v sol water—Et,A" [193°] Formed by the action of methylamine on dimethyl pyrone dicarboxylic ether, which is obtained from cupric acetoacetic ether and COCl. Needles (Gerichten, B 19, 25, Conrad a Eckhardt, B

OXY-METHYL-PYRIDYL-PROPIONIC ACID v. Ecconine.

OXY-DI-METHYL PYRIMIDINE

[192°] Formed from acetamidine hydrochloride, acetoacetic ether, and dilute (10 p c) NaOHAq (Pinner, B 18, 2845, 29, 1616). Needles, v e sol ordinary solvents

Ethyl derivative [55°] (259°) Prisms Oxy-tri-methyl pyrimidine

 $CMe <_{N}^{N} \underset{C(OH)}{CMe} > CMe$ Formed from acet amidine hydrochloride, methylacetoacetic ether, and dilute NaOHAq (Pinner, B 22, 1617) Needles, v sol water

D1-oxy methyl-pyrimidine

CO<NH CMe NH CO NH CO NH CH Methyl uracıl Formed by boiling β uramido crotonic acid with acids (Behrend, A 229, 8, 231, 256) Needles (from alcohol) Decomposes at 270°-280° By heating with potash it is converted into C10H12I2N4O5 Potash and MeI at 140° forms a dihydride C₅H₈N₂O₂ [219°] and di-oxy-tri methyl pyrimidine A mixture of PCl₅ and POCl₂ at 125° forms only C₈H₃Cl₃N₂ (246°), SG 218 1 6273 Yields deep violet coffin-like crystals of di iodide $C_5H_6N_2O_2I_2$ (Hoffmann, A 253, 74)

Di-oxy tri methyl-pyrimidine

CO < NMe CO > CH [109°]Formed by methylation of the preceding body (Behrend, Hagen, A 244, 2) Plates, v sol water and alcohol, sl sol ether Yields methylamine on heating with baryta water at 200° Dry Br forms C₈H_uNO₄Br₂, aqueous bromine yields $CO < NMe CMe(OH) > CBr_2 [163^{\circ}],$ whence boul ing alcohol gives brome oxy tri methyl pyr imidine [126°], converted by cone aqueous ammonia into oxy amido tri-methyl pyrimidine $\rm CO < \stackrel{NMe}{NMe} \stackrel{CMe}{CO} > C NH_2$ [167°], a body that is changed by potassium cyanate and HCl into crystalline $CO < NMe CMe CO > C NH CO NH_2$.

OXY-METHYL-PYRROLE Dihydride ÇH, CO ČH₂ CHMe>NH γ Amido valeric lactam [37°] Formed by heating γ amido valeric acid and by the action of sodium amalgam and HOAc at 280° on the phenyl-hydrazide of levulic acid (Tafel, B 20, 250, 22, 1862) Yields an only nitrosamine, which produces valerolactone on distillation -B'HCl [110°] Needles, v sol water -B',H2PtCl

ν Oxy-di methyl pyrrole C.H.NO 1.6 CH CMe NOH Made by heating its carboxylic acid (Knorr, A 236, 302) Reduces silver solution in the cold and Fehling's solution on boiling Gives a red substance with acids, and exhibits the pine-wood reaction

Oxy-tri-methyl-pyrrole ? C,H,,NO methyl-pyrrolone (175°) SG 2 945 Formed from sodio ethyl cyanide and MeI (Hanriot a. Bouveault, Bl. [8] 1, 175)

Di-oxy-tri-methyl pyrrole v. Acetoramines, vol. i. p. 27.

OXY.METHYL.PYRROLE CARBOXYLIC ACID CO NH CMe Ethyl ether EtA'. [134°] Formed by heating a-amido-ethylidene-

succinic ether at 150° (Emery, A 260, 144) Needles, v sol alcohol Yields an acetyl derivative [142°]

Oxy - d1 - methyl - pyrrole carboxylic acid Ethyl ether CO CHMe C CO2Et [127°] Formed from methyl acetosuccinic ether and alcoholic NH, at 0° (Emery, A 260, 151) Small white prisms (from HOAc)

Oxy-di-methyl-pyrrole carboxylic acid Ethyl sther CO NMe CMe
(160° et 11 ---) [42°] (160° at 11 mm) Formed from acetosuccinic ether and alcoholic methylamine (E) Bunches

of needles, v sol ether

Oxy-di-methyl-pyrrole carboxylic acid C,H,NO, to N(OH) CMe CH Formed by boiling oxy di methyl pyrrole dicarboxylic ether with NaOHAq (Knorr, A. 236, 301) Slender needles, v sol alcohol Gives off CO₂ at

Oxy-di-methyl-pyrrole dicarboxylic acid N(OH) CMe C CO₂H

Mono-ethyl ether EtHA" Formed by boiling the di-ethyl ether with alcoholic potash (Knorr, A 236, 299) Crystals (from alcohol) Decomposes at 185° into CO2 and oxy-dimethyl pyrrole carboxylic ether

Diethyl ether Et2A" [99°] Formed by heating di acetyl succinic ether with hydroxyl amine hydrochloride, NaOAc, and HOAc (Knorr) Yields the salt C12H16KNO

OXY METHYL - PYRROLE DIHYDRIDE CARBOXYLIC ACID Nitrila

CH, CH, CM CN [141°] Formed by heat ing CH, CO CH, CH, CO, Et with HCy and am monia in a closed tube (Kuhling, B 22, 2369, 23, 708) Octahedra (from hot alcohol) Suc cessive treatment with cold H2SO, and water converts it into the corresponding amide [161°] Hydroxylamine yields the amidoxim [156°]

OXY - METHYL - PYRROLE DIHYDRIDE THIOCARBOXYLIC AMIDE

CH₂ CH₂ CMe CS NH₂ [220°] Formed by passing H₂S through an ammoniacal solution of the nitrile of oxy methyl pyrrole dihydride carb oxylic acid (Kuhling, B 22, 2370) Prisms (from hot water), almost insol alcohol

OXY-METHYL-QUINAZOLINE

 $C_{\bullet}H_{\bullet} < N = 0$ Anhydro-acetyl o-amido - CMe benzamide [233°] Formed from acetyl o amido benzamide by the action of heat, alkalis, or boiling water (Weddige, J pr [2] 36, 143)
Silky needles (containing aq), v sol hot aloo
hol MeI and KOH yield the methyl derivative $C_{\bullet}H_{\bullet}N_{\bullet}(OMe)$ [109°] $-B'HCl -B'_{\bullet}H_{\bullet}PtCl_{\bullet}$.

Oxy-methyl-quinasoline

CH CHCC(OH) N [238°]. Formed from o-∸ĊH CMe CH C N_amido-p-toluic amide and formic acid (Niemen towski, J pr [2] 40, 12). Crystals, insol water.

Oxy-di-methyl-quinazoline C10H10N2O re C_eH_sMe<CO NH N CMe [255°] Formed by boiling o amido-p toluic amide with Ac.O (Niementowski, \tilde{B} 21, 1534, J pr [2] 40, 13) Needles (from boiling water), sol acids and alkalis

Oxy-di methyl-quinazoline

CeH CO-N [199°] Formed by heating acetyl o amido benzamide above its melting point (Weddige, J pr [2] 36, 154) Cry (containing 3aq), v e sol alcohol —B'HCl Crystals

D1-oxy-methyl quinazoline CH CH C CO NH (?) Formed by heating amido m-toluic acid with urea at 180° (Niementowski, J pr [2] 40, 21) White needles (from amyl alcohol), insol benzene Not melted at 300° HI and P yield o toluidine

Di oxy methyl-quinazoline C₆H₄ NH CO

Formed by heating C₆H₄(NH₂) CO NHMe with urea at 200° (Abt, J pr [2] 39, 147) Long white needles, sl sol hot water

Di-oxy-methyl quinazoline C₆H₄ CO NH CO Formed by heating

C₆H₄(NHMe) CO NHCO₂H with urea (Abt) Di-oxy-di-methyl quinazoline

 $U_6H_4 < CO NMe CO$ [151°] Formed by the action of MeI and NaOH on either of the two preceding bodies or on di oxy quinazoline (Abt, J pr [2] 39, 145) White needles (from water), v sol alcohol

Oxy methyl-quinazoline dihydride

C₆H₄< [120°] Formed by boiling woxy tolyl methyl thio urea with yellow HgO Soderbaum a Widman, B 22, 2936) Needles, v e sol methyl alcohol —B'₂H₂PtCl₆ B'HAuCl₄ [185°] Yellow prisms [203°]

OXY-METHYL QUINIZINE v OXY PHENYL-METHYL-PYRAZOLE

(B 1, 4)-OXY METHYL-QUINOLINE

CH CMe C_{P} C_{P} C_{P} [263°] Formed from the amido compound and HNO₂ (Noelting a Trautmann, Bl [3] 4, 244), and by fusing (B 4) methyl quinoline (B 1)-sulphonic acid with NaOH (Herzfeld, B 17, 905, 1551) Needles (from dilute alcohol) Yields a nitroso deriva tive C₉H₄Me(NOH)(OH)N [200°] By KOH, MeI, and MeOH it is converted into the methyl derivative C₁₀H₈(OMe)N (c 230°), whence B'2H2PtCl

 $(B \ 4, 1)$ Oxy-methyl-quinoline

CH CMe CH C(OH) C₅H₃N [124°] Formed by heating amido p-cresol (10 g) with glycerin (24 g), H₂SO₄ (20 g), and pieric acid (2 g) (N a T) Needles, v sl sol cold water Dyes fabrics mordanted with alumina, yellow

(B 4, 2)-Oxy methyl-quinoline

CMè CH $CH \cdot C(OH) > C_5H_5N$ [96°] Formed from the amido- compound by the diazo- reaction (N a T) Formed also by fusing the sulphonic acid with NaOH (O Fischer a Willmack, B 17, 441, Hersfeld, B. 17, 1552) Needles (from chloro-

form) Smells like vanilla. Its alcoholic solution is coloured green by FeCl, Yields a nitrosodeuvative [200°] - B'2H2PtCl, 2aq orange needles

Methyl derivative UnH, NO Oil — B'2H2PtCl64aq brown crystalline pp

Tetrahydride C.H.Me(OH) < NH CHG Formed by reduction with tin and HCl Needles or plates, sl sol water Yields a nitrosamine C10H12(NO)NO crystallising in small yellow needles

(B 4, 3) Oxy-methyl-quinoline

CH, CH $_{\rm CMe}\;\widetilde{c({\rm OH})}{>}{\rm C_5H_8N}$ Formed from amido o crésol hydrochloride (10 g), glyceiin (24 g), H_2SO_4 (20 g), and pieric acid (2 g)(Noelting a Trautmann, B 23, 3663) Needles (from dilute alcohol), volatile with steam FeCl, gives a dark green coloui Mixed with CuO it colours a flame green Yields a crystalline p nitroso derivative decomposing at 200° without melting

 $(B^2, 4)$ -Oxy-methyl quinoline

C(OH) CH CMe>C,H,N [200°] Formed by soda fusion from o toluquinoline sulphonic acid (Herzfeld, B 17, 903) Needles Not volatile with steam FeCl, colours its alcoholic solution brownish red

(B 1, 2) Oxy-methyl quinoline

CMe C(OH) CH Ana oxy paratoluquinol [230°] Formed from the amido com inepound, and also from para toluquinoline by sul phonation (with 25 p c SO₃ extra) at 90° and potash fusion (Noelting a Trautmann, B 23, Needles, v sl sol hot water Not vola tile with steam

(Py 3, 1) Oxy methyl quinoline $C_0H_4 < N = C(OH)$ [224° cor] ([224° cor] (above 360°) Formed by heating the anilide of acetoacetic acid with H SO, (Knoir, A 236, 83, C J 46, 334, Roos, B 21, 624, Reissert, B 24, 855) Small needles (from water) Reduced by sodium amalgam to C₂₀H₂₀N₂O₂ [280°] Sodium added to its alcoholic solution reduces it to a dihydride C₁₀H₁₁NO [101°] and methyl quinoline tetrahy dride $C_{11}H_{18}N$ (253°) NaOEt and MeI form oxydi-methyl quinoline [132°] and the methyl deriva tive C₁₆H₈(OMe)N [276° cor], whence B' H₂PtCl₆ The ethyl derivative C₁₆H₈(OEt)N [51°] (250°) is formed from chloro lepidine and KOEt

Salts -B'HCl $[187^{\circ}]$ —B'₂H₂PtCl₆ aq -B'H₂SO, needles —B'HNO, prisms —B'HI — Picrate [166°] Needles —Ba(C₁₀H₈NO), aq. (Py 3, 4) Oxy methyl quinoline

 C_eH_{\bullet} < CH CH COMethyl-ψ carbostyril [72°]. Formed by digesting carbostyril with MeOH and MeI, adding NaOH as required to neutralise the HI formed (Friedlander a Muller, B 20, 2010) Slender needles Weak base Sodium amalgam forms $C_{10}H_{10}NO$ [276°] — B'H₂PtCl₆2aq — B'HgCl₂ [189°] Small pyramids

Methylo-rodide B'MeI Bronzed needles

(Py 1, 3) Oxy methyl-quinoline

 $C_eH_4 < N = CMe^*$ [[231°] (above 360°) in the cold, 10 at 100° Formed by heating phenylamido crotonic ether rapidly to 240° (Conrad a Limpach, B 20, 947) Prisms (containing 2aq), v sol alcohol Tastes bitter FeCl, colours Prisms (containing its solution yellowish-red KMnO, oxidises it to scetyl nthranilic acid Yields quinaldine on distillation with zinc dust —B'HCl —B'₂H₁PtCl₈ [215°] $-B'H_{,}CrO_{,}$ [108°] $-B'C_{o}H_{,}(NO_{,})$ OH [200°] Yellow needles

Methyl derivative C10H8(OMe)NO [82°] (296°) Formed from chloro methyl quinoline, MeOH, and NaOMe at 135° Needles, al sol

water Methylo chloride C₁₀H₀NOMeCl aq [217°] Formed from the methylo iodide and AgCl (Conrad a Eckhardt, B 22, 74) -B'2H2PtCl

[240°] Yellow crystalline pp Methylo vodide C₁₀H₂NOMeI aq Formed from the base and MeI at 100° [240°] [201°] Sating

needles (from hot water)

[283°]. Sulphonic acid C₁₀H₈NO(SO₃H) Long prisms (containing 2aq) -BaA'2 4aq

 $(B \ 2)$ -Oxy- $(Py \ 1)$ methyl quinoline C(OH) CH C CMe CH CH = CH C N = CH [218°] Formed fusing lepidine sulphonic acid with NaOH (Busch a Koenigs, B 23, 2684) Obtained also by boiling with HBrAq the methyl derivative which is produced by heating quinine sulphate (40 g) with KOH (95 g) and water (45 cc) at 220° in a current of superheated steam (Koenigs, B 23, 2674) Groups of slender needles, v sol warm alcohol and acetone Gives no colour with FeCl,

Methyl derivative CHHINO [52°] Formed as above, and also by heating quinene zinc chloride with water at 200° Slender needles (containing aq) Its solution fluoresces like quinine Gives a bluish green colour with ammonia and chlorine water - B'2H2PtCla

[237°] Orange powder

Oxy (Py 1) methyl-quinoline[141°] Formed from a sulphonic acid of lepidine prepared by mixing lepidine with H₂SO₄ and heating to 300° (Busch a Koenigs, B 23, 2686) Greenish needles, v sol benzene —B'₂H₂PtCl₆ 2aq orangeyellow needles

 $(B \ 2)$ Oxy $(Py \ 3)$ methyl quinoline

C(OH) CH C CH CH p Oxy quinaldine

CH —CHC N CMe p Oxy quantitative [213°] Formed by the action of parallehyde and HCl upon p amido-phenol, and also by fusing (Py 3) methyl quinoline sulphonic acid with potash (Doebner a Miller, B 17, 1708) Crystals, not volatile with steam, v sl sol cold water -B'2H2PtCle 2aq yellow needles

 $(B\ 2\ ?)$ Oxy $(Py\ 3)$ methyl-quinoline f₃Me(OH)N [234°] Formed by C.H.Me(OH)N Formed by fusing quinaldine (\$\beta\$) sulphonic acid with potash (D a M) Silvery plates, sol ether and hot alcohol, nearly insol hot water—B'HCl2aq— B'2H,PtCl, 2aq small yellow needles

(B 4)-0xy (Py 3) methyl-quinoline CH CH— C CH CH CH C(OH) C N CMe o Oxy quinaldine [74°] (266°) Formed by fusing (Py 3) methylquinoline (B 4)-sulphonic acid with potash, and also by the action of paraldehyde and HCl on o amido phenol (Doebner a Miller, B 17, 1705). Trimetric prisms, easily volatile with steam.

B'_HPtCl_ 2aq yellow needles

Vol. III

methyl derivative
[125°] (282°) Formal C_oH_oMe(OMe)N Formed from o anisidine, par-

aldehyde, and HCl —B',H.PtCl, yellow needles Tetrahydride C,H,Me(OH)N (280°) Formed by reducing o oxy quinaldine with tin and HCl (Doebner a Miller, B 17, 1706) Yields $C_9H_9Me(OMe)N$ (270°) whence B $\acute{H}Cl$ and $C_9H_9Me(OMe)NMe$ (261°), whence $B'_2H_2PtCl_6$. yellow needles

(B 2) Oxy (Py 4)-methyl quinoline tetra-hydride Methyl derivative C₉H₂NMe(OMe) Methyl thallırı (278°) Formed by methylation of thallırı (Skraup, M 6, 776) Oil — B'H₂SO₄ — B'MeI aq [224°] — B'₂Me₂PtCl_• Orange plates

 $(\vec{B} \ \vec{4})$ Oxy $(Py \ \vec{4})$ methyl quinoline

Tetrahydride C₁₀H₁₂NO ve CH CH—C CH₂ CH₂ [114°]

[114°] Formed from CH C(OH) C NMe CH2 (B - 4) oxy quinoline tetrahydride and MeI (O Fischer, B 16, 714) Trimetric tables (from ether) a b c = 631 1 1 538 Its alcoholic solution is coloured brown by FeCl,—B'HCl aq
Kairine, a febrifuge—B MeI [216°] Prisms
(from MeOH)—B'C,H,Cl (312°) Oil (Fischer
a Kohn, B 19, 1040, C J 49, 503)

Methyl derivative C,H,(OMe)NMe (257) Formed by means of MeI and MeOH Pale yellow oil Gives a crimson colour with NaNO2 and a little acid -B' H2PtCl, [1990] -

B'H.SO, prisms, v sol water

Methyl derivative of the methylosodide C.H. (OMe)NMe I [175°] (from MeOH) Moist Ag₂O converts it into strongly alkaline crystalline C₀H₀(OMe)NMe₂OH, whence {C₉H₀(OMe)NMe Cl}₂PtCl₄ [200°]

Ethyl derivative C.H. (OEt)NMe

at 716 mm Oıl

(Py 3) Oxy (B 2) methyl quinoline

CMè CH C CH CH Methyl carbostyril [228°] CH CHCNHCO Formed by boiling chloro methyl carbostyril with NaOHAq (Einhorn a Lauch, A 243, 359) Crystalline, v sol alcohol

(B 1,2,4) Oxy di methyl quinoline

CMe C(OH) C CH CH [198°] Formed by the CH CMe CN CH action of nitrous acid on (B 12,4) amido di methyl quinoline (Noelting a Trautmann, B 23,

Plates (from chloroform), v sol alcohol $(\dot{P}y \ 3,1,4)$ Oxy-di methyl quinoline $C_{11}H_{11}NO$

S. C.H. CHE CH Methyl lepidone methyl-ψ carbostyrıl [132°] (290° at 250 mm) Formed by heating (Py 3,1) oxy methyl quin-oline with KOH and MeI, or by heating the isomeric methoxy lepidine above its boiling point (290°) Formed also by heating methylaniline with acetoacetic ether, and treating the product with H.SO. (Knorr, B 17, 2876, 19, 3501, A 236, 104) Needles, al sol water and ether, v sol alcohol, insol alkalis Sodium amalgam reduces it to (C, H, NO), [268°] -B', H, PtCl, dag [214°] Slender needles

 $(\tilde{P}y \ 1,3,4)$ Oxy di-methyl-quinoline

Co CH NMe CMe [175°] Formed from methoxy methyl quinoline by heating at 315° in a sealed tube, or by heating oxy quinaldine methylo iodide with NaHCO, (Conrad, B 20, 956, 22, 75) Needles, v sol water -B'HHgCl.

[187°] Needles —B'.H.PtCl. [240°],—B'MeI [2100] SI sol cold water

 $(\bar{P}y$ 3,2,1) Oxy di methyl quinoline

C_oH₄ CMe CMe [262°] Formed from methylacetoacetic amilide and H2SO4 in the cold (Knorr, A 245, 357) Yields a sulphonic acid, which forms a crystalline Ba salt Ba(C11H10NSO4)2-B'HCl Long silky needles

(B 2)-Oxy (Py 1,3) di methyl quinoline

Ç(OH) CH C CMe ÇH [214°] (above 360°) CH = CH C N = CMe Formed by heating p amido phenol hydrochloride (1 vol) with acctone (3 vols) for some days at 175° (Engler a Bauer, B 22, 213) Prisms or tables, v sl sol water FeCl. colours its alco holic solution brown —B'HCl.—B'2H2PtCl, 2aq —B'2H2SO, —B'2H2Cr2O, —B'C,H2(NO2),0H

 $(B \ 4)$ -Oxy $(Py \ 1.3)$ di methyl-quinoline

CH CH — C CMe CH [65°] (281° uncor) ČH C(OH) C N CMe Formed in like manner from o amido phenol Prepared by saturating a mixture of acetone (3 mols) and paraldehyde (3 mols) with dry HCl, adding, after 3 days, o amido phenol (2 mols) dissolved in conc HClAq, and heating on the water bath Crystals, v sol alcohol, ether, and benzene FeCl, colours its alcoholic solu-tion green --B'H₂SO₄ --B'HCl.-B'₂H₂PtCl₆ 2aq --B'₂H₂Cr₂O₇ --B'C₆H₃N₃O₇ [207°] Plates or prisms, sl sol hot alcohol

(Py 3)-Oxy-(B 2 Py 1)-di-methyl-quinoline CMe CH C CMe CH [250°] Formed from CH CH CN = COH acetoacetic ether by successive treatment with p toluidine and H₂SO₄ (Knorr, A 245, 365) Flat prisms, sl sol hot water, dilute acids, and al kalis Yields (B 2, Py 1)-di methyl-quinoline

on distillation with zinc dust

(Py 3) Oxy (B 8, Py 1) di-methyl-quinoline CH CH C CMe CH [220°] Formed in like CMe CH C N = C OH manner from m toluidine (K) V sl sol hot Yields (B 3, Py 1)-di methyl quinoline on distillation with zinc dust -Platinochloride [234°] The hydrochloride is crystalline,

and is decomposed by water
(Py 3)-0xy-(B 4; Py 1) dimethyl quinoline
ÇH CH C OMe ÇH

Formed in like monner Formed in like manner CH CMe CN_COH from o toluidine (Knorr, A 245, 368) Slender needles (from water) Yields (B 4, Py 1) di-

methyl-quinoline on distillation

B'₂H₂PtCl₂2aq [220°] —NaC₁₁H₁₀NO Plates ($\stackrel{.}{P}y$ 1) 0xy ($\stackrel{.}{B}$ 2, $\stackrel{.}{P}y$ 3) di-methyl quinoline CMè ČH Ć C(OH) ÇH [275°] Formed by CH=CH C N = ---- CMe heating p tolyl amido crotonic ether

C,H,NH CMe CH CO,Et at 250° (Conrad a Lim pach, B 21, 525, cf Knorr, B 17, 542) Needles (containing aq)—B'HCl Needles (from hot Needles (from hot [228°] Prisms (from hot water) -B'2H2PtCla water)

(Py 1)-0xy-(B.4, Py.3)-di methyl quinoline CH CH—C C(OH) CH CH CMe C N—— OMe [261°] Formed by distilling o-tolyl amido-crotonic ether (C a L) Plates (containing aq) —B'₂H₂PtCl₂ Needles

Oxy-(Py 1, 3)-di-methyl-quinoline C₁₁H₁₀N(OH) [44°]. Made from (Py 1, 3) di-

methyl-quinoline by conversion into the sulphonic acid and fusing this with NaOH (Beyer, J pr [2] 33, 409) —(B'HCl)₂PtCl₄2aq

Oxy-tri-methyl quinoline

CMe CH CC(OH) CH CH CMe CN CMe [264°] Formed by heating m xylyl β amido crotonic ether (Conrad a Limpach, B 21, 526) Needles (containing aq) —Platinochloride [282°] Needles

Oxy tetra methyl-quinoline C, H, NO te $C_6HMe_3 < N = CMe$ Formed by quickly heat ing ψ-cumyl amido crotonic ether at 250° (Conrad a Limpach, B 21, 529) Prisms (from alcohol) Sublimes at 285°, without previous fusion -B'2H2PtCl, Prisms (from alcohol)

(Py 1, 3, 4) Di oxy-methyl-quinoline

 $C_{\epsilon}H_{\epsilon} < \begin{array}{c} C(OH) CH \\ NMe CO \end{array}$ [260°] Formed by heating its methyl derivative with HClAq at 120° Small needles, sol alkalıs Yields a nitrosamine C₁₀H₈NO₂(NO) crystallising in red needles [c

Methyl derivative C.H. COMe CO [68°] Formed by heating (Py 1, 3, 4) chloro oxy methyl quinoline with NaOMe (Friedlander a Muller, B 20, 2014) Slender white needles, v sol alcohol −B'₂H₂PtCl₆ pyramids Ethyl derivative C₁₀H₈(OEt)NO [87 5°]

Slender white needles

(B 4, Py 1) Di oxy-(Py 3) methyl quinoline Methyl derivative CH CH _ —С C(OH) ÇН [229°] Formed by CH C(OMe) C N ____CMe heating o methoxy phenyl amido crotonic ether at 260° (Conrad a Limpach, B 21, 1654) Long silky needles (containing aq) — B'2H2PtCl6 Tables

 $(B\ 2, Py\ 1)$ -Dı oxy $(Py\ 3)$ methyl-quinoline Methyl derivative C(OMe) CH C C(OH) CH [290°] Formed by CH ====CH C N= =CMe the action of heat on p methoxy phenyl amido crotonic ether which is made from p anisidine and acetoacetic ether (C a L) -B'HCl - $B'_2H_2PtCl_6 - B'_2H_2SO_4$ S 6 in the cold - B'MeCl [251°] Needles $-B'_2Me_*PtCl_64aq$ -S 6 in the cold -B'MeI Converted by moist Ag2O into C12H12NO2 [149°]

Di-methyl derivative C_pH₄Me(OMe)₂N

o] Formed from the methyl derivative, [94°] NaOMe, and MeI Needles or prisms

(B 2, 3)-Di oxy-(Py 3) methyl quinoline Methylene derivative

CH₂ < O C CH C CH CH CH CH . [152°] Formed on reduction of

CH₂O₂ C₆H₂(NO₂) CH CH CMe N₂HPh (Haber, **B** 24, 623) Silvery needles, m sol ether—
B'_2H_PtCl_s—B'H_CrO_ Detonates at 210°—
Picrate [175°] Yellow crystals
(Py 1, 2, 3, 4) - Tri - oxy - methyl - quinoline

C₄H₄ C(OH) C(OH) Dr-owy-methyl-pseudo carbostyril Formed by warming the nitrosoderivative of (Py 1, 8, 4)-di-oxy methyl-quinoline with SnCl₂ White needles, sl sol water, benzene, and CHCl. By Fe₂Cl, it is oxidised to methyl-pseudo-quinisatin

co co [122°] (Friedlander a Muller, NMe CO B 20, 2015)

References - Bromo, Chloro, and Di-CHLORO DI NITRO- OXY METHYL QUINOLINES

(B 4) OXY (Py 4) METHYL QUINOLINE CARBOXYLIC ACID Tetrahydride C,H,Me(OH)(CO,H)N [211°] (S a E), [216°] (K a N) Formed by heating oxy quinoline carboxylic acid tetrahydride with MeI and MeOH at 120° (Schmitt a Engelmann, B 20, 1219, Krolikovsky a Nencki, M 9, 208) Prisms (containing 2aq), v sol hot water and alcohol Has no toxic action After administration to dogs the urine contains the acid C.H.Me(OH)2(CO2H)N [255], insol water

(B 4) Oxy-(Py 3) methyl quinoline carb-lic acid $NC_9H_4Me(OH)(CO_2H)$ [207°] oxylic Formed by heating potassium oxy quinaldine with liquid CO₂ at 190° (König, B 21, 883) Yellow needles (containing aq), sl sol cold water Gives a cherry red colour with FeCl,

(Py 1) Oxy-(Py 3) methyl quinoline (Py 2)carboxylic acid $C_6H_4 < N = C(OH) C(CO_2H)$

Formed by oxidising the corresponding aldehyde with alkaline KMnO₄ (Conrad a Limpach, B 21, 1975) Ciystals (from alcohol) -MgA'2 (dried at 100°) Crystalline pp

(Py 3, 1)-0xy-methyl quinoline (B 4) carboxylic acid [312°] Formed by oxidising (a) oxy (γ) methyl julole dihydride with KMnO₄ in acid solution (Reissert, B 24, 853) Needles, m sol alcohol, sl sol hot water

 $(Py \ 1)$ OXY $(Py \ 3)$ METHYL QUINOLINE (Py 2) CARBOXYLIC ALDEHYDE

 $C_6H_4 < N = CMe$ [273°] Formed, together with $C_{31}H_{23}N_3O_3$ [192°], by boiling (Py 1, 3) oxy methyl quinoline with chloroform and KOHAq (Conrad a Limpach, B 21, 1972) Yellow plates (from alcohol), sol acids and alkalis —B'HCl —B',H-PtCl₆ [215°-220°]

Phenyl hydrazide C1,H13N3O-B'HCl

yellow needles, sl sol hot water

 $(Py \ 1) \ 0xy \ (B \ 1, 2, 4, Py \ 3)$ tetra methyl quinoline $(Py \ 2)$ carboxylic aldehyde

CMe CVe CC(OH) C CHO CH CMe—CN ——CMe Formed by the action of caustic soda and chloroform on the corresponding oxy tri methyl quinoline (C a L) Yields, with phenyl hydrazine hydrochlor ide, crystalline C. M., OHCl

OXY METHYL QUINOXALINE

ÇH CHÇNÇH Oxytoluquinoxaline ČM€ CH Ö N Č OH Formed by oxidation of its dihydride by the air or by ammoniacal AgNO, (Hinsberg, B 19, 483, Feebly basic plates PCl, yields A 248, 75) chloro methyl quinoxaline [77°]. — NaA' aq

plates, sol water.

Methyl derivative [71°] Ethyl derivative [67°] From the chloro methyl quinoxaline and NaOEt Satiny needles

Dihydride C₂H₁₀N₂O [95°-124°] Formed by reducing o nitro tolyl amido acetic acid with tin and HCl (Plöchl, B 19, 10, Leuckart a Hermann, B 20, 27) Formed also from chloro acetic at the 20, 27 acetic ether and tolylene o-diamine (Hinsberg, B 18, 2870) Very oxidisable.

Oxy di methyl quinoxalıne

 $C_0H_3Me < NCMe$ [238°] Formed by pass ing air through an alkaline solution of the dihydride, which is obtained by condensing tolyl ene o diamine with a bromo propionic or pyruvic acid (Hinsberg, A 237, 351, 248, 78) crystals (from alcohol), v sl sol water Is perhaps a mixture of isomerides

Dihydride C₆H₃Me<NH CHMe [c 135°]

Crystallises from alcohol.

Oxy-tri methyl quinoxaline Dihudride C₆H₃Me < NH CMe₂ [227°] Formed by heat ing tolylene o diamine with bromo isobutyric ether (Hinsberg, A 248, 79) Plates, v sl sol Yields an acetyl derivative [206°], a nitrosamine [154°], and a di-nitro compound [above 280°]

Dı oxy-dı methyl-quinoxaline Ds-ethyl CH C(OEt) C N CMe CH C(OEt) C N CMe derivative [127°]

Formed by the action of di methyl-diketone (diacetyl) on the hydrochloride of the di ethyl derivative of (a) di amido-hydroquinone (Nietzki a Rechberg, B'23, 1212) Long yellow needles D1-oxy-d1-methyl-d1quinoxaline, so called,

ÇMe NCCHÇNÇMe Formed by the action C(OH) N C CH C N COH of NaOAc and pyruvic acid in excess on a solu tion of the hydrochloride of tetra amido benzene (Nietzki a Muller, B 22, 445) Dissolves in alkalis with greenish yellow fluorescence

OXY METHYL QUINOXALINE CARBOXY-LIC ACID $C_{10}H_8N_2O_3$ to $C_6H_3(CO_2H) < N CMe$ Formed by adding pyruvic acid in slight excess to an aqueous solution of di amido benzoic acid (Zehra, B 23, 3629) Pale yellow needles, m sol hot alcohol Blackens above 300° without

melting —Ba A'₂ 3aq yellowish white needles
Oxy-methyl-quinoxaline carboxylic acid $C_{b}H_{a}Me < N \stackrel{C}{C} \stackrel{CO_{2}H}{C}$ Formed by the action of boiling potash on C₁₁H₁₀N₄O₃ [258°], which is made by mixing aqueous solutions of alloxan and tolylene o diamine (Hinsberg, A 237, 356) Yellow needles (from dilute alcohol) Gives off CO2 at 214°

OXY-METHYL SUCCINIC ACID v OXYPYBO-TARTARIC ACID

Oxy di methyl succinic acid v Oxy adipic

Di oxy di methyl succinic acid CO,H CMe(OH) CMe(OH) CO,H Dr methylracenic acid [179°] Formed by saponifying its nitrile with HClAq Crystals (containing aq) -KHA" Plates, m sol hot water -CaA"1aq -BaA''2aq small needles

Nutrile CN CMe(OH) CMe(OH) CN. [c 110°] Formed from di methyl di ketone (diacetyl) and HCy (Fittig, A 249, 208) Very hygroscopic needles, sl. sol chloroform

Isomeride -DI-METHYL TARTARIO ACID OXY METHYL-TEREPHTHALIC ACID C.H.Me(OH)(CO.H), [2 5 4 1] [285°-290°] Formed by fusing C.H.Me(SO.NH.)(CO.H), with potash (Jacobsen a H Meyer, B 16, 191). [285°-290° Minute prisms (from very dilute alcohol), decomposed on fusion.

. . .

S C(OH) CH CMe N. OXY - METHYL-THIAZOLE

Thiocyanacetone [102°] Formed by heating the carboxylic acid (Wohmann, A 259, 298), or by heating with dilute HClAq the compound CH₂CO CH₂SCy, formed from chloro acetone and a sulphocyanide (Tscherniak a Norton, $C\ J\ 44,568$, Hantzsch, $B\ 20,3127,3337$, 21, 941, $A\ 249,20$) Needles Yields methyl thiazole on distilling with zinc-dust With phenylene m diamine it forms C₆H₄(NH C₄H₄SN)₂ [152°] Reacts with hydroxylamine

 $\frac{S-CO}{CH,CO}$ NMe Di - oxy - methyl - thiazole Formed from di oxy thiazole, NaOMe, and MeI (Arapides, A 249, 28) Liquid, v e sol water Decomposed by boiling NaOHAq into methyl amine and thioglycollic acid C₂H₂Cl₂NOS [161°] PCl, yields

OXY-METHYL THIAZOLE CARBOXYLIC

ACID SCOH N [222°] Formed from its C(CO,H) CMe ether, and also by heating chloro methyl thiaz ole carboxylic acid with cone KOHAq (Zurcher, A 250, 286, Wohmann, A 259, 296) Plates or needles (containing xaq), v sol water — NH₄A'5aq Prisms, decomposing at 138°

Ethyl ether EtA' [129°] Formed toge-

ther with (SC, Me(CO, Et)N), O [142°] from chloroacetoacetic ether and ammonium or barium sulphocyanide (Hantzsch a Weber, BSilky plates Hydroxylamine forms 3132)

 $C_{10}H_{10}O_{b}N_{4}S_{2}$ [c 217°]

OXY METHYL-THIOPHENE SCHOOL CH Formed from levulic acid and P.S. (Kues, B 19, 555) Oil, sl sol water —B'HOAc (210°) Yellow oil

OXY METHYL UREA Di-ethyl derivative of the glycollyl derivative CH₂(OEt) NH CO NH CO CH₂ OEt [80°1 Formed from CH₂(OEt) CONH₂, bromine, and potash (Hofmann, B 18, 2736) Needles (from water)

OXY-METHYL XANTHINE C6H8N4O3 16 at 16° Formed by the action of potassium cyanate on the hydrochloride of di oxy amidomethyl pyrimidine CO< $\stackrel{\rm NMe}{\rm NH}$ $\stackrel{\rm CH}{\rm CO}>$ C $\stackrel{\rm NH}{\rm C}$ (Beh rend, A 231, 252, Lehmann, A 253, 80) Needles or prisms (containing 2aq), sl sol water Does not reduce alkaline AgNO

OXY-MYRISTIC ACID [51°] C14H28O2 Occurs in the essential oil from the fruit of Angelica archangelica (Muller, B 14, 2480) Pearly plates (from alcohol) —KA' aq —CuA', AgA' bulky pp Benzoyl derivative [68°]. AgA'

(1,2) DI OXY NAPHTHALENE

 $C_{10}\dot{H}_{6}(\dot{O}H)_{2}[1\ 2]$ [60°] v (\$\beta\$) Hydronaphtho-QUINONE, vol n p 728

(1,4) Di-oxy-naphthalene [176°] v (a) Hydro-NAPHTHOQUINONE

[260°] (1,4') Di-oxy-naphthalene py potash fusion from (a) naphthol sulphonic acid and from naphthalene (1,4')-disulphonic acid (Erdmann, A 247, 356, Bernthsen, B 20, 938, Armstrong a Wynne, C J Proc 3, 43) Scales, v sol hot alcohol, sl sol water Yields erystalline C₁₀H_s(OAc)₂ [160°]

Pera di oxy-naphthalene C₁₀H₆(OH)₂[1 17] [140°] Formed by potash fusion from the anhydride got by boiling naphthylamine persulphonic acid with water (Erdmann, A 247, 357) Needles or plates, sl sol water Yields C₁₀H₆(OAc)₂ [148°] crystallising in white plates

Di-oxy-naphthalene Made by reducing peri naphthoquinone with HOAc and zinc-dust (Mel dola a Hughes, C J 57, 631) Minute needles which blacken at 205° Yields C₁₀H₈(OAc), [227°] According to theory, this body should

be identical with the preceding

(1,2')-Dioxynaphthalene [178°] Formed by fusing (8) naphthol (a) sulphonic acid (Bayer, B 15, 1351) with potash (Emmert, A 241, 371) Needles, v e sol alcohol, m sol water Its alkaline solution blackens quickly FeCl, gives a blue pp Y_1 $C_{10}H_6(OEt)_2$ [67°] Yields C₁₀H₆(OAc), [108°] and

(1,3') Di-oxy naphthalene [135°] Made by potash fusion from naphthalene (1,3') di sul phonic acid (Ewer a Pick, G P 45,229 [1887]) or (3) naphthal (a) sulphonic acid (Claus, J pr [2] 39, 315) White prisms (from benzene) Turns red in air FeCl, gives a blue colour

Yields $C_{10}H_6(OAc)$, [73°]

(2,3') Di-oxy naphthalene [216°] Formed by potash fusion from naphthalene (2,3') di sul phonic acid (Dusart, Bl [2] 8, 200, Darmstadter a Wichelhaus, A 152, 306) and from (B) naphthol (β) sulphonic acid (Schaffer, A 152, 298, Armstrong a Graham, C J 39, 140, Emmert, A 241, 369) Thin plates, v sol alcohol, sl sol cold water Gives a yellowish white pp with FeCl₃ Yields C₁₀H₆(OAo)₂[175°] and C₁₀H₆(OEt), [162°] Forms a disulphonic and which gives BaC₁₀H₆S₂O₈ 2aq (Griess, B 13, 1959)

(2, 2') Di oxy naphthalene [190°] Formed by potash fusion from naphthalene (2,2') di sulphonic acid (Ebert a Merz, B 9,609, Weber, B 10, 1233, 14, 2206, Clausius, B 23, 519) Needles (from hot water) Its alkaline solution blackens in air Yields $C_{10}H_6(\text{OAc})_2$ [136°], $C_{10}H_6(\text{OBz})_2$ [139°], $C_{10}H_6(\text{OMe})_2$ [134], and $C_{10}H_6(\text{OEt})$ [104°] (Liebermann, B 15, 1428)

Dioxynaphthalene [161°] Got by fusing (β) naphthol (R) disulphonic acid (1 pt) with NaOH (4 pts) at 310°, or by heating with dilute (25 p c) H, SO, at 200° ($E\ P\ 15,803$) Crystals (from water) FeCl₂ gives an intense blue colour Combines with diazo compounds

Tri oxy naphthalene $C_{10}H_8O_3$ Got by reducing oxy (a) naphthoquinone (Graebe, A 154, 324) Yellow needles (from ether) Very readily oxidised

DI-OXY-NAPHTHALENE DICARBOXYLIC ACID C₁₀H₄(OH)₂(CO₂H)₂ [162°] Formed by heating narceic acid (Claus a Mexner, J pr [2] 37, 1) White needles, v sol ether Yields 37, 1) White needles, v sol ether Yields $C_{10}H_{e}(CO,H)_{2}$ [253°] on reduction $-Na_{s}A''6aq$ $-NaHA''5_{2}aq$, small needles -BaA''2aq $-Ag_{s}A''$

DIOXYNAPHTHALIC CtoHsO. ACID [126°] Made by boiling chloro oxy naphthalic acid (v Naphthalene) with baryta (Hermann, A 151, 67) Prisms -KHA" aq -BaA" 3aq -Ba(HA")₂. — Ba(NH,A")₂ 2aq — Ca(NH,A")₃. — Cu(NH,A")₃. blue prisms

DI-OXY-NAPHTHAZINE C16H10N2O. 300° | Formed from di oxy naphthoquinone and naphthylene-(1, 2) diamine in alcohol (Nietzka Basterlik, B 24, 1339). Reddish brown needles, si sol alcohol

(α) ÓXY (β)-NAPHTHOIC ACID

C₁₀H_c(OH)CO₂H [F2] Naphthol carboxylic acid [187°], S 058 at 17° Formed by passing CO₂ over sodium a naphthol at 100° (Eller, A 152, 277, Schaffer, A 152, 291, Nietzki a Gie termann, B 20, 1274), or by heating sodium-(a)-naphthol with liquid CO₂ at 130° (Schmitt Burkard, B 20, 2699) Stellate groups of needles (from alcohol) FeCl, colours its solution blue PCl, forms C₁₀H₆(OPOCl₂) CCl,

[115°], whence most air forms $C_{10}H_4(O\ PO(OH)_2)\ CO_2H$, while alcohol yields $C_{10}H_6(O\ P(OEt)_2)\ CO_2H\ [63°]$ (Wolffenstein, B 21, 1186) —NaA' 3 aq —NaA' —NH $_4$ A' —PhA'

C₁₀H₆(OAc) CO₂H Acetyl derivative [158°]

Methyl ether MeA' [78°] Converted by hydroxylamine into C₁₀H₆(OH) CO NH(OH)

Ethylether EtA' [49°]
Phenylether PhA' [96°]
Methyl derivative of
C₁₀H₆(OMe) CONHPh [218°] the anilide Made from methyl (a) naphthol, phenyl cyanate, and AlCl, (Leuchart a Schmitt, B 20, 2340) Prisms

(β) 0xy (α) naphthoic acid $C_{10}H_6(OH)(CO_2H)$ [2 1] [15 [157°] Formed, in like manner, from (B) naphthol (S a B, cf Kauffmann, B 15, 804) Slender needles, decomposing at 125° when slowly heated pletely decomposed by boiling water into CO_2 and (β) -naphthol FeCl, gives a blue colour PCl, yields $C_{10}H_6(\mathrm{OPOCl})\mathrm{COCl}$ [38°], whence moist air forms C₁₀H₆(OPO(OH)₂) CO₂H [156°], while dilute alcohol produces

 $C_{10}H_6(OPO(OEt))CO_2H$ [113°] (Rabe, B 22) yellow needles, m sol cold 392) —NH,A' water

Methyl ether MeA' [76°] Converted by hydroxylamine into amorphous $C_{10}H_6(OH)$ CO NH(OH) [178°] (Jeaurenaud, B

Ethylether EtA' [55°]

of the amide Methyl derivative C, H (OMe) CONH. [186°] Form from methyl (8) naphthol, AlCl₃, and ClCONH₂ (Gat termann, A 244, 75) Crystals (from alcohol)

of the amiae EthylderivativeC₁₀H₆(OEt) CONH₂ [161°]

cohol)

Methyl derivative of the anilide H_c(OMe) CONHPh [169°] Made from C₁₀H₆(OMe) CONHPh methyl (β) naphthol and phenyl cyanate in presence of AlCl, (L a S) Needles

(β) Oxy-naphthoic acid $C_{10}H_6(OH)CO_2H$ [? 2 3'] [216°] Formed in small quantity from sodium (8) naphtholand CO at 290° (Schmitt a Burkard, B 20, 2702) Plates, v sol alcohol Very stable FeCl, colours its solution blue Its methyl ether does not react with

hydroxylamine

Peri-Oxy-naphthoic acid C₁₀H₄(OH)CO₂H[1 1'] [169°] Made by heating its internal anhydride for a long time with dilute KOHAq (Ekstrand, B 19, 1138, J pr [2] 88, 278) Small needles (from ether), v sol Solutions of its salts are coloured violet by FeCl. — CaA', 8 aq decomposed on boiling

Anhydride C, H, CO Naphtholactone.

[108°] Made from amido (a) naphthoic acid by the diazo reaction Needles (from alcohol) or tables (from ether), insol cold aqueous alkalis

(a)-Oxy-naphthoic acid C₁₀H₆(OH) CO₂H [1 4?]

Ethyl derivative C10H6(OEt)CO2H. [214°] Formed by the action of alcoholic potash on the amide C₁₀H_c(OEt)CONH₂ [244°], which is made from C10H, OEt and ClCONH, in presence of AlCl₃ (Gattermann, B 23, 1198, A

244, 73) Needles, m sol alcohol — NaA'3aq.
plates — CaA'23aq needles, sl sol water

Methyl derivative CloH₃(OMe) CO₃H.
[232°] Formed, in like manner, from

H (OM) CO₃NH. (C242) which is reconstituted. C₁₀H₆(OMe) CONH₂ [234°] which is prepared

from C₁₀H,OMe

(a)-Oxy (a) naphthoic acid [234°-237°] Formed by fusing (a) sulpho (a) naphthoic acid [235°] with potash (Battershall, \hat{A} 168, 114) Needles (from water), v sol alcohol Aqueous solutions of its salts blacken on boiling

gives a dirty violet pp
(α)-0xy-(β) naphthoic acid [213°] Made by potash fusion from sulpho (8) naphthoic acid Needles (from boiling water)
Its stable FeCl, gives a dirty red pp
(β) Oxy (α) naphthoic acid [Its salts are un-

[247°] by potash fusion from the sulpho naphthoic acid [218°-222°] (Stumpf, A 188, 6) Mass of needles (from water) FeCl, has no effect in the cold, but gives a brown pp on warming

(β) Oxy (α) naphthoic acid [187° Made by potash fusion from sulpho-naphthoic acid [182°-185°] (Stumpf) Branching needles (from Gives a chocolate colour with FeCl. water) Yields (3) naphthol on distilling with lime

(B) OXY NAPHTHOIC ALDEHYDE C₁₀H₆(OH)CHO [76°] Aldehydo naphthol Formed from (B) naphthol, chloroform, and aqueous NaOH (Kauffmann, B 15, 805, 16, 683). Prisms (from alcohol), almost insol water FeCl, colours its solution brown Reduces warm ammoniacal AgNO, forming a mirror With Ac.O and NaOAc it forms C₁₀H₄(OAc) CH(OAc). 124°] Yields, on oxidation, oxy-naphthoic acid [150°]—CleH₆(ONa) CHO yellow plates

(a) OXY (a)-NAPHTHOPHENAZINE

CleH₁₆N O te ClH₄ N₂ CleH₅OH [4 3 1] Formed by heating (a) amido or diethylamido- (a)-

naphthophenazine with conc HClAq for 5 hours at 180° (Fischer a Hepp, B 23, 845, Eicker, B 23, 3805) Reddish yellow needles (from alcohol) The hydrochloride forms red prisms with green lustre

OXY-(β) NAPHTHOQUINOLINE C, H, NO Formed by fusing (β) -naphthoguinoline sulphonic acid with potash (Gentil, B 18, 202)

Does not melt below 250°

(a) OXY-(a)-NAPHTHOQUINONEU JUGLONE. (β) -Oxy-(a) naphthoguinone $C_{10}H_a(OH)O_{2}$ Naphthalic acid [190°] Formed by heating amido- or oxy- naphthoquinonimide or oximidonaphthol with HGlAq or alkalis (Martius a. Griess, A 134, 377, Graebe a Ludwig, A 154, 321, B 4, 970, Merz a Diehl, B 11, 1814, kehrmann, B 23, 2453) Formed also in like manner from phenyl-amido (a)-naphthoquinone and from phenyl amido-(β) naphthoquinone (Baltzer, B 14, 1900, Zincke, B 14, 1496, Liebermann a. Jacobson, A 211, 80) Yellow needles, v sl sol cold water May be sublimed

Reactions —1 Reduced by tin and HCl to tri oxy-naphthalene—2 The Na salt heated with o-phenylene-diamine forms (a)-naphthoeurhodol (Kehrmann, B 23, 2453) —3 Benzow eurnodol (Renrmann, B 25, 2453)—3 Benzove allehylde forms CHPh(O₁H₂(OH)O₂)₂ [211°–214°] (Zincke, B 21, 2203)—4 Phenyl-hydrazme yields O₁₀H₂(OH)O(N₂HPh) [230°] which forms the salts CaA'₂ 4aq and BaA'₂ 10aq, the ethers MeA' [175°] and EtA' [173°], and the acetyl-derivative C₁₀H₁₁AcN₂O₂ [179°] It reacts with allehylde observed electrons and sectors. with aldehyde, benzoic aldehyde, and acetone, forming C₈,H₂₈N₄O₄ [c 258°], C₈₅H₂₈N₄O₄, and C₃₆H₄₆N₄O₄ [245°-250°] respectively (Zincke a Thelen, B 17, 1812, 21, 2205)—AgO₁₀H₅O₃. scarlet needles (from hot water)

Ethyl ether EtC₁₀H₅O₅ [127°] Needles Imide v Amido naphthoquinone

Anilide v Phenyl amido naphthoquinone Oxim C₁₀H₅(NOH)(OH)O [1 2 4] Nitroso naphtharesorcin Formed from oxy-naphtho quinone and hydroxylamine (Kostanecki, B 22, 1843) Needles, decomposing at 180° Gives with ferrous salts a green, and with ferric salts a dark-brown lake The hydrochloride forms yellow needles Nitrous acid C10H4(NOH)2O2 crystallising in plates (containing aq), decomposing at 165°

 $\mathbf{Oxy} \cdot (\boldsymbol{\beta})$ -naphthoquinone $C_{10}H_{5}(OH)O_{2}[2' \ 1 \ 2]$ Formed by oxidising its oxim with FeCl, Red-

dish brown, amorphous pp, v sol alcohol
Oxim C₁₀H₃(OH)(NOH)O [2' 1 2] [235°] Formed from (2,2') di oxy naphthalene and nitrous acid (Clausius, B 23, 521) Brownishyellow needles

Di-oxy-naphthoquinone C₁₀H₄(OH)₂O₂ Naph thazarm Formed by heating di intro naph thalene [214°] with zine and H₂SO, at 200° (Roussin, De Aguiar a Baeyer, B 4, 251, 438, Liebermann, B 3, 905, A 162, 330) Reddish brown needles with green lustre, v sl sol boiling water, v sol alcohol Its alkaline solution is Its solution in H2SO4 is crimson Barytaand lime- waters give violet blue pps

Isomeride v Oxy Jugione, p 101

Di oxy-naphthoquinone C,0H4(OH),O2 Formed by heating oxy amido naphthoquinone with HClAq at 175° (Merz a Diehl, B 11, 1322) Reddish-brown needles (from alcohol) Its alkaline solution is brownish-violet Dyes violet with alumina mordants and dark blue with iron Dyes silk brownish violet with me tallic lustre It forms a crystalline di acetyl derivative —BaA" —PbA" —Ag₂A", greenishblue pp

Tri-oxy-naphthoquinone A black by product in preparing naphthazarin (Aguiar, B 4, 439) References - Bromo- and CHLORO- OXY NAPH-

THOQUINONE

OXY - NAPHTHOQUINONE SULPHONIC ACID C10H2(OH)O2SO3H Formed by the action of alkalis on the acid C10H4(OH)(SO3H)(OSO3H)2 got by dissolving dichloro naphthoquinone in aqueous KHSO, (Graebe, A 149, 9) - K2A" (dried at 140°) · orange crystals

References — Bromo- and Chloro- oxy NAPH-

THOQUINONE SULPHONIC ACID

(β)-OXY-0 NAPHTHOYL-BENZOIC ACID C₁₀H₄(OH) CO C₂H₄ CO₂H Phenyl oxy-naph-Prethoul-ketone-o-carboxulic acid [256°]

pared by oxidising an alkaline solution of (\$\beta\$). dioxy-dinaphthyl with KMnO, (Walder, B 16, 299) Silky prisms Sol alcohol, ether, and acetic acid, nearly insol water

Reactions -1 On fusion with KOH i' gives (β) naphthol and phthalic acid —2 Heated with HI it is reduced to (β) -oxy ω naphthyl o-tolube acid $(C_{10}H_0(OH) CH_2, C_0H_1, CO_2H) -3$ Heated with $ZnCl_2$ to 220° it yields a substance $C_{30}H_0$. Or which forms colourless crystals [146°], easily soluble in alcohol -4 Heated with resorcin it gives a red colouring matter, and with dimethylanılıne and ZnCl₂ a green

Salts -A'Na white crystalline powder, sl sol cold water and alcohol -A'Ag insoluble pp -A'2Ba 2aq slightly soluble white pp

Methyl ether A'Me [199°], prisms Ethyl ether A'Et [206°], needles Acetyl derivative C18H11O3(OAc) [170°] DI (a) OXY DINAPHTHYL

 $\mathbf{C}_{10}\mathbf{H}_{6}(\mathbf{OH})\ \mathbf{C}_{10}\mathbf{H}_{6}(\mathbf{OH})$ Dinaphthol[300°] Formed by adding FeOl, to a cone solution of (a) naphthol (Dianin, B 6, 1252, 7, 125, 187, Julius, Chem Ind 10,97) Silvery plates (from alcohol), insol water Its alcoholic solution is coloured red by FeCl.

Bensoyl derivative C₂₀H, (OB2)₂ [253°] Dr-methyl ether C₂₀H, (OMe)₂ [251°] Dr ethyl ether C₂₀H₁₀(OEt)₂ [211°] Pearly plates (Ostermayer a Rosenhek, B 17, 2453)

D1-(3)-oxy (aa) dinaphthyl [218° cor] V D 9 52 (obs) Prepared by oxidation of an ethereal solution of (3) naphthol with FeCl, the yield being 60 pc of the theoretical amount (Dianin, Walder, B 15, 2166) Needles or (Dianin, Walder, B 15, 2100)
plates Gives with FeCl, a greenish colour,
plates on heating on heating with H,SO. ZnCl₂ it gives (3) dinaphthylene oxide forms $C_{20}H_{10}(OH)_{2}(SO_{3}H)_{2}$, whence BaA''6aq, $C_{20}H_{10}(OH)_{2}(SO_{3}H)_{4}$ is also formed ZnCl, and NH, at 330° form $C_{20}H_{13}N$ [157°], which forms a picrate [217°] and an acetyl derivative [144°] -Picrate C20H14O22O6H2(NO2)3OH [1740] White crystals, sol alcohol

Benzoyl derivative C.H. (OH)(OBz) [204°]

Di benzoyl derivative C20H12(OBz)2. [160°]

D₁ methyl ether C₂₀H₁ (OMe) [190°] D₂-ethyl ether C₂₀H₁₂(OEt)₂ [90°] Di-oxy dinaphthyl [195°] A product of

the action of melted potash on (3) naphthoic aldehyde (Kauffmann, B 15, 807) Silky needles (from alcohol)

Tetra oxy-dinaphthyl C., H₁₀(OH), 'Dinaphthyl dihydroquinone' [178°] Formed by reduction of the quinone C₂₀H₁₀O₄ (Stenhouse a Groves, C J 33, 415), and by the action of tin and HCl on (3) naphthoquinone (Korn, B 17, 3024) Colourless needles, darkening by oxida tion in air, insol water, v sol HOAc The The quinone $C_{20}H_{10}O_4$ is exidised in alkaline solution by the air to [4 8 2 1] $O_{10}H_4O_2(OH)$ $O_{10}H_4O_2(OH)$ [1 4 3 2] [245°-250°]

Acetyl derivative C₂₀H₁₀(OAc), [1 a OXY-(a)-NAPHTHYL-ACETIC ACID C₁₂H₁₀O₂ is C₁₀H, CH(OH) CO₂H. (a)-Naphthyl-glycollic acid [93°] Formed by reducing (a)-naphthyl glyoxylic acid with sodium amalgam (Boessneck, B 16, 640) Formed also by saponifying its nitrile (Brandis, B 22, 2153), and from (a) naphthyl methyl ketone by successive treatment with bromine and potash (Schweizer, B 24, 549) Rosettes of needles (from water) Yields (a) naphtheic aldehyde on oxidation with

dilute HNO, —BaA', —AgA' pulverulent pp Methyl ether MeA' [79°] Needles Nutrale CleH, CH(OH) CN Formed from (a)-naphthoic aldehyde, KCy, and cold HClAq

Oil, v sol alcohol

a-Oxy-(8) naphthyl-acetic acid [158°] (S), [c 176°] (C a T) Prepared in the same way as its isomeride (Claus a Tersteegen, J pr [2] 42, 518, Schweizer, B 24, 547) Small needles (from water) Reduced by HIAq to C₁₀H₂CH₂CO₂H re 142°7

[75°] Nec-Methyl ether MeA' Needles Ethyl ether EtA' [87°] C10H, CH(OAc) CO2H Acetylderivative

[150°]

Amide C₁₀H, CH(OH) CONH₂ [228°] Oxy di-naphthyl acetic acid C₂,H₁₄O₂ $(C_{10}H_7)$ C(OH) CO_2H Yellowish green tables, decomposing about 100°

Anhydride C22H12O2 Formed by heating (a) naphthol with exalic acid and H2SO, (Heenig, M 1, 251) Pale red plates, sl sol chloroform

(8) OXY-NAPHTHYL-ACRYLIC ACID C₁₀H₆(OH) CH CH CO₂H [170°] Formed by heating its anhydride with aqueous potash at 170° Crystalline powder, sol alcohol

Anhydride C10H6 CH CH (β)-Naphthocoumarin [118°] Prepared by heating (3)oxy-naphthoic aldehyde (2 pts) with Ac₂O (10 pts) and NaOAc (2 pts) at 180° (Kauffmann, B Needles, v sol alcohol, sl sol hot

An isomeride of this anhydride [141°] is got by heating (\$\textit{\beta}\$) naphthol with malic acid and \$H_2SO_4\$ (Pechmann a Welsh, \$B\$ 17, 1651) OXY-DINAPHTHYLAMINE \$\varphi\$. IMDO DI-

NAPHTHYL OXIDE

Tri oxy (B) naphthylamine

C₁₀H₄(OH)₅(NH₂)[1 3 4 2] Formed from nitro oxy quinone, SnCl., and HCl (Kehrmann a Weichardt, J pr [2] 40, 181) Brownish violet needles—B'HCl monoclinic prisms

Tetra-acetyl derivative [145°] (B) OXY-NAPHTHYL-CROTONIC

Anhydride C10H6CMe CH [162°] Formed by the action of H2SO4 on a mixture of acetoacetic ether and (B) naphthol (Pechmann a Cohen, B 17, 2190) Needles, sol alcohol solution in H.SO, exhibits green fluorescence DI-OXY-NAPHTHYLENE-DIAMINE

 $C_{10}H_4(OH)_2(NH_2)_2[1 8 2 4]$ Formed by the action of SnCl, and HCl on the oxim of oxyamido naphthoquinone (Kehrmann a Weichardt, $J pr [2] \bar{4}0, 186$ Its alkaline solutions become crimson on oxidation, and then blue on boiling -B'HCl white needles

TRI-OXY-TRI-NAPHTHYL ETHANE

CloHe(OH) CH. CH(CloHe OH). Formed from di-chloro di-ethyl oxide and (a) naphthol (Wislicenus, A 243, 165) White amorphous powder, insol water, sol alcohol

(a) OXY-NAPHTHYL ETHYL RETONE CteH. (OH) CO CtH, [81°] Formed by heating (a)-naphthol with propionic acid and ZnCl, at 178° Pale yellow plates (from ether or alcohol).

Phenyl hydraside [128°].

Methyl ether [58°] Formed from propoonyl chloride, C₁₀H,OMe, and AlCl, (Gattermann, B 23, 1209) Prisms (from ether).

Yields an oxim C₁₀H,(OMe) C(NOH) C.H. [172°].

OXY.NAPHTHYL METHYL KETÖNE

[1 3]C, H, (OH) CO CH, 'Ketonaphthol' [168°] Formed by the rapid distillation of phenyl aceto isocrotonic acid (Erdmann, A 254, 197) Crystals (from dilute alcohol)

Acetyl derivative C14H12O2 [109°]

Oxim C₁₂H₁₁NO₂ [174°]

Oxy naphthyl methyl ketone [103°] Formed by heating (a)-naphthol with HOAc and ZnCl, Witt, B 21, 321) Pale-green six sided prisms from benzene) Its alkaline salts are yellow (from benzene) Alcoholic NH, at 200° forms

C₁₀H_e(OH) C(NH₂) CH₃ [203°]

Oxim C₁₀H_e(OH) C(NOH) CH₃. [170°]

(a) Oxy-naphthyl methyl ketone Probably identical with the preceding isomeride Methyl ether C₁₀H₆(OMe) CO CH₂ [72°] (above 350°) Formed from C₁₀H₇(OMe), AcCl, and AlCl₂ (Gattermann, B 23, 1208) Six sided tables

Ethyl ether C₁₀H₆(OMe)Ac [79°]

(3) Oxy naphthyl methyl ketone Methyl

ether C₁₀H₂(OMe) CO CH₂ [58°] Formed from C₁₀H₂OMe, AcCl, and AlCl₂ (G) Slender needles

Ethyl ether [63°] Compact tables OXY (a) NAPHTHYL METHYL PYRAZOLE C14H12N2O 2 6 C10H, N COOH CH [c 190°] Formed by heating (a) naphthyl hydrazine with acetoacetic ether at 130° (Knorr, B 17, 551) Yields a methyl derivative [129°] (a) Naphthyl hydrazine and thio acetoacetic ether form C24H18N4O [220°] (Sprague, C J 59, 343)

[190°] Oxy- (β) naphthyl methyl-pyrazole Yields a methyl de Formed in the same way rivative [129°

(a) OXY-NAPHTHYL PROPYL KETONE C₁₀H₆(OH) CO C₂H₇ [78°] Formed by heating butyric acid with (a) naphthol and ZnCl. (Goldzweig, J pr [2] 43, 97) Silky needles (from ether), m sol hot water

DI - OXÝ - DI - (a) - NAPHTHYL - PYRAZINE HEXAHYDRIDE

C₁₀H,N<C(OH) CH Č(OH)>NC, [275°] Formed by boiling the acetyl derivative of chloro (a) naphthylamine with alcoholic potash (Abe nius, J pr [2] 40, 437) Formed also by heat

ing (a)-naphthylamido acetic acid with Ac.O at 200° (Bischoff, B 22, 1807, 23, 2003) Plates (from HOAc), insol alkalis

Di-oxy-di (8) naphthyl-pyrazıne hexahydride [above 360°] Formed by heating (\$)-naphthyl amido acetic acid at 220° in hydrogen, and by the action of chloro acetic ether on the naph thalide of (3) naphthylamido acetic acid (Bis choff) Plates, sol aniline Converted by boil-

ing alcoholic potash into

O_{1e}H.NH CH₂CO N(C_{1e}H₁)CH₂CO₂H [105°]
DI-OXY-DI (β) NAPHTHYL SULPHIDE
S(C_{1e}H₂OH)₂ Naphthol sulphide [215°]
Formed, together with the di- and tri- sulphides SULPHIDE by the action of sulphur at 180° in presence of PbO, or of S.Cl. in benzene, upon $(\hat{\beta})$ -naphthol (Tassinari, \hat{G} 17,94, Onufrovitch, \hat{B} 21,3559, 23, 3355). Prisms, insol water, ether, and benzene, m sol hot alcohol Yields di oxy dinaphthyl on heating with powdered copper NH, Aq forms, on heating, (8) naphthylamine oholic and ammoniacal AgNO, forms $H_{12}SO_2$ [164°]—Na₂A'' 6aq needles Acetyl derivative $SC_{20}H_{12}(OAc)$, [154°] Alcoholic C20H12SO2

Benzoyl derivative [2080] Plates

Ethyl ether SC₂₀H₁₂(ÖEt)₂ [189°] Yields a di-nitro derivative [235°]

D1-oxy d1 (3) naphthyl d1sulphide

 $8_2(C_{10}H_6OH)_2$ [169°] Formed as above Thin yellow needles, m sol benzene Yields di oxy dinaphthyl on heating with Cu at 240°

Di-acetyl derivative S2C20H12(OAc)2

[c 140°] Yellowish crystalline mass

Di bensoyl derivative [187°]

Di-ethylether [158 5°] Needles Di oxy di-naphthyl disulphide S₂(C₁₀H₆OH) [210°] Formed by heating (β) naphthol with NaOHAq and S (Lange, B 21, 260) Needles, insol water, v sol HOAc It is accompanied by the preceding isomeride [170°]

Di-oxy di-(β)-naphthyl trisulphide

S_s(C₁₀H₆OH)₂ Formed as above (Onufrovitch) Powder Yields a dibenzoyl derivative [194°]

ν ΟΧΥ-(α)-NAPHTHYL-THIO UREA C,H,NH CS NH(OH) [116°] Formed from (a) naphthyl thiocarbimide and hydroxylamine (Tiemann, B 22, 1939, Voltmer, B 24, 382) Pearly plates (from alcohol), insol. water Hot sloohol converts it into (a) naphthyl cyanamide

Benzyl ether C10H,NH CS NH(OCH2Ph) [183°] Formed by using benzyl hydroxyl amine

(β)-OXY ω NAPHTHYL o TOLUIC $C_{10}H_6(OH)-CH_2-C_6H_4CO_2H$ [261°] Formed by reduction of oxy naphthoyl benzoic acid by heating with HI and P to 200° (Walder, B 16, 304) Small colourless prisms Nearly insol water, sl sol alcohol and ether —A'Ag floccu lent pp

OXY-NITRO v NITRO OXY

DI-OXY-OCTANE $C_8H_{18}O_2$ \imath e

CPrH(OH) CPrH(OH) Mol w 146 [515°] (223°) Formed by the action of alcoholic potash on isobutyric aldehyde (Fossek, M 4, 664, 11, 397) Monoclinic tables, v sol alco Combines with CaCl₂ Yields isobutyric and oxalic acids on oxidation by HNO3 Boiling dilute H_2SO_4 forms a (β) pinacolin $C_{16}H_{12}O_2$ (162°) Conc H_2SO_4 in the cold forms an (a)-pinacolin $C_8H_{16}O$ (122°) smelling like camphor

Acetyl derivative $C_8H_{16}(OAc)_2$ (235°) Octylene glycol Di oxy-octane $C_9H_{16}(OH)_2$ (285°-240°) S G $^{\circ}$ 932 Obtained from octylene bromide by successive treatment with AgOAc and solid KOH (De Clermont, C R 59, Oil, sol alcohol

Acetyl derivative CaH16(OAc)2 (245°-250°

Di-oxy-octane CMeEt(OH) CMeEt(OH) Methyl ethyl-pinacone [c 28°] (200°-205°) A product of the action of sodium amalgam on methyl ethyl ketone (Lavrinovitch, A 185, 124) Crystalline mass, m sol water

Tri-oxy-octane

OMePr(OH) CH, CH(OH) CH,OH (210° 60 mm) Formed by the action of HOCl followed by KOH upon methyl allyl propyl car binol (Reformatzky, J pr [2] 40, 412) Thick

liquid, v. sol water and alcohol, sl sol alcohol.

Yields a liquid tri acetyl derivative

Tetra oxy-octane C,H, (OH), v e CH, (OH) CMe(OH) CH, CH, CMe(OH) CH, OH [154°] Formed by the action of water on the liquid C₈H₁₄O₂ (170°-180° at 125′ mm) which is produced by the action of potash on C_sH₁₄ClO(OH), a body formed by the addition of oxygen and HOCl to CH2 CMe CH2 CH2 CMe CH2 (Przybytek, B 20, 3242)

DI OXY OCTENOIC LACTONE

 $CH_2 CH CH_2 C(OH) < CH_2 CHMe$ Formed by the action of conc H₂SO₄ on (C₃H₅)₂C(OH) CO H [48°] (Bulitsch, J pr [2] 39, 94) syrup Yields amorphous Ba(C₈H₁₃O₄),

OXY OCTINOIC ACID C,H12O, 1 e C(C₃H₅)₂(OH) CO₂H 'Diallyloxalic acid' [48°] Formed by saponifying its ether, which is made by the action of zinc and allyl iodide on oxalic ether (Saytzeff, A 185, 183, Schatzky, J pr [2] 34, 485, Bl [2] 45, 183) Needles, m sol LnA'aq —BaA'₂ —CaA'₂2aq —ZnA'₂1¹aq S (of ZnA'₂) 28 at 22° —CdA'₂aq —PbA'₂2aq —CuA'₂ minute green needles

Ethyl ether EtA' (2136° cor)

9873, 15 9718

Methyl derivative C(C,H_s). (OMe)CO₂H Yields the salts BaA'₂2aq —PbA' 0¹aq —CuA' aq and the ether EtA' (216°) SG ²⁰ 9607 $\mu_{\beta} = 1 \ 4556 \quad R_{\infty} = 89 \ 52 \quad (Barataeff, \ J^* \ pr \ [2]$ 35, 1

Heptic acid [151°], obtained by the action of bromine and potash on isobutyl acetoacetic ether (Demarçay, A Ch [5] 20, 472), is perhaps an oxyoctinoic acid It yields CaA', 5aq, crys tallising in needles

 α OXY-OCTOIC ACID $\mathrm{C_8H_{16}O_3}$? eCPr₂(OH) CO₂H [73°] (K a S), [81°] (R) Formed by the action of zinc and propyl iodide on oxalic ether (Rafalsky, B 14, 2068, Bn 1, 527) Formed also by heating butyroin with conc KOHAq (Klinger a Schmitz, B 24, 1273) Needles—KA'—BaA' scales
Ethyl ether EtA' (209° cor) Oil

α-Oxy-octoic acid CPr2(OH) CO2H [111°] Formed from its ether, which is made from oxalic acid, isopropyl iodide, and zine (Markownıkoff, Z [2] 6, 516) Needles (from water), volatile with steam - BaA'2 3aq, small efflorescent needles

(203° cor) Oil Ethyl ether EtA'

a-Oxy octore acid

CH₂Pr CH₂ CH₂ CH(OH) CO₂H [69 5°] Formed from cenanthol and HCy, followed by boiling HClAq (Erlenmeyer a Sigel, B 7, 697, 1108, A 177, 102) Plates, v sl sol water Split up by HClAq at 120° into cenanthol and formic acid.

Ethyl ether EtA' (230°) at 715 mm

Amide [150°] Satiny plates

S G 17 905 Netrele C.H. CH(OH) CN Formed from cenanthol and anhydrous HCy in the cold Liquid, sl sol water a-Oxy-octoic acid CMe, CH, CMe(OH) CO,H.

[107°] A product of the oxidation of 'isodibutylene' with KMnO₄ (Butleroff, J R 1882, 190, C J 42, 936, Bl [2] 88, 554) Needles or prisms, v sol hot water -AgA' needles

8-0xy octoic acid CH, CH(OH) CEt, CO,H | Formed by reducing diethyl acetoacetic ether with sodium amalgam and water (Schnapp, A 201, 62) Hygroscopic syrup, v sol alcohol, m sol water Decomposed on distillation into aldehyde and dı ethyl acetic acıd —NaA'26aq -CpC,H,O, -AgA' flocculent pp

β Oxy octoic acid CH, CH(OH) CMePr CO H Formed by reducing methyl propyl acetoacetic ether (Jones, A 226, 288) Split up on distilla tion into aldehyde and methyl propyl acetic

acid - ZnA', crusts

B Oxy octoic acid CPrH(OH) CMe CO H [108°] Formed by reducing isobutyryl isobutyric ether (Wohlbruck, B 20, 2334, Hantzsch, A 249, 54) Prisms, v sol ether —BaA'₂3aq

γ Oxy octoic acid CEt₂(OH) CH₂ CH₂ CO₂H Formed from succinyl chloride and ZnEt,

B 15, 1852) Oil, v sol alcohol and ether

γ Oxy-octore acid

CH₃ CH(OH) CMeH CEtH CO₂H Formed by reducing acetyl hexoic acid (Young, C J 43, 177, A 216, 43) —BaA'₂ amorphous Lactone C₈H₁₄O (227°)

y Oxy-octoic acid Lactone C,H,O2 (134° at 36 mm) A product of the action of sodoform or rodine on NaOCH2Pr (Gorboff, J pr [2] 41, 236, 261) Liquid

Oxy octoic acid [92°] A product of the action of alcoholic potash on isobutyric aldehyde (Fossek, M 4, 676) Crystals —CaA'₂ sol

water

Di oxy-octoic acid

CHMe(OH) C(CH Pr)(OH) CO H A product of the action of alcoholic potash on biomo iso butyl acetoacetic ether (Demar, xy, C = R = 86, 1135) Liquid, m sol water - BaA' needles -CaA'.

Di oxy octoic acid

(CHMe(OH) CH.) CH CO H Formed by boiling barium di oxy di propyl malonate with water (Hjelt, A 216, 70) Anhydride C₈H₁₄O₃ Liquid, v e sol water

Tri oxy octoic acid Lactone

CH, CH(OH) CH C(OH) < CH₂ CHMe Formed

by the action of H2SO, on a oxy octoic acid [47°] (Bultsch, J pr [2] 39, 89) Syrup, sol alcohol -Ba(C,H15Os).

Tetra oxy octoic acid C,H1,O, tc

(CH₂(OH) CH(OH) CH₃)₂CH CO H boiling tetra oxy di propyl malonic acid with baryta water (H) Readily changes to the only anhydride CaH, O,

Penta-oxy-octoic acid

(CH,(OH) CH(OH) CH,)2C(OH) CO2H Lactone CaH14O4 Formed by heating a-oxyoctore ('diallyl oxalie') acid with nitric acid on a water bath (Bulitsch, J pr [2] 39, 65) Yellow liquid, v sol water and alcohol, insol ether

References -Bromo- and DI CHLORO

OCTOIC ACID

DI-OXY OCTYLENE O.H,4(OH)2 Conyleneglycol Acetyl derivative C.H. (OAc)2 (225°) S.G. 199 9887 Formed by convlene bromide and AgOAc (Wertherm, A 130, 298)

OXY-OLEIC ACID C, H,O, An only product of the action of Ag.O on dibromostearic acid (Burg a Overbeck, A 140, 69) An isomeric acid [58°]

is formed by the action of H2SO, on oleic acid (Liechti & Suida, B 16, 2455)

OXY-OXALACETIC ETHER Ethylderivative CO2Et CH(OEt) CO CO.Et (155°at17mm) Formed by the action of sodium ethylate on a mixture of oxalic ether and CH2(OEt) CO2Et in ether (Wislicenus a Scheidt, B 24, 432) Thick liquid, miscible with alcohol and ether

 α OXY-PALMITIC ACID $C_{18}H_{32}O_{2}$ Formed by boiling a broino palmitic acid with alcoholic potash (Hell a Jordanoff, B 24, 939) Small crystals (from alcohol)

Acetyl derivative [62 5°]

OXYPARACONIC ACID C,H,O, An acid formed by boiling calcium chloroitamalate with water (Morawski, J pr [2] 11, 450) Thick lıquıd —CaA', 2aq rhombohedra

TETRA OXY PENTAMETHENYL HYDRIDE

 $_{\text{CH(OH)}}<_{\text{CO CH}_2}^{\text{CO CH(OH)}}$ Formed by the action of HOAc on the Ba salt of its carboxylic acid (Hantzsch, B 20, 2792) Oil—BaA"3½aq amorphous powder, almost insol water

Carboxylic acid $CH(OH) < CO CH CO_2H$

Formed from ammonium trichloro di oxy hexenoic acid and baryta water at 60°— BaA'24aq bulky pp, insol water

OXY PENTANE v AMYL ALCOHOL.

Di-oxy pentane CH2(CH CH2OH)2 104 (260°) Formed from pentamethylenediamine by \'HNO_2 (Gustavson, J pr [2] 39, 542)

Dı oxy-pentane CHMe(OH) CH₂ CH₂ CH₂(OH) (220°) at 713 mm S G ⁰₆ 1 0003 Formed by reducing acetopropyl alcohol by sodium amalgam (Fieer a. Perkin, C J 51, 836, B 19, 2568, Lipp, B Liquid, miscible with water, decom-236° HBrAq at 100° forms an an-22. 2567) posing at 236° hydride (78° at 716 mm), and finally C₅H₁₀Br₂

Di-oxy pentane CHEt(OH) CHMe(OH) (187 5°) SG $\frac{9}{6}$ 9945, $\frac{19}{6}$ 9800 Formed from the corresponding di bromo pentane by succes sive treatment with AgOAc and baryta water (Wagner a Saytzeff, A 179, 308) also by heating the oxide OCHEt with water at 100° (Eltekoff, J R 1882, 355) Yields a oxy butyric acid on oxidation

D1 oxy pentane CHPr(OH) CH2(OH) (206°). S G 2 999 Formed from the corresponding dibromo pentane (Flavitzky, B 10, 230, 2240, A 179, 351) Yields oxy valeric acid on oxidation P.O. forms valeric aldehyde and methyl iso-

propyl ketone

CMe2(OH) CHMe(OH). D1-oxy pentane 8 G º 987 Made from the corresponding di bromo pentane (Wurtz, A Ch [3] 51, 458) Formed also by heating methyl isopropenyl carbinol with dilute H2SO, (Kondakoff, J R 20, 32) Syrup, with bitter taste Misoible with water, alcohol, and ether Yields oxy-180butyric acid on oxidation Yields methyl-isopropyl ketone when heated at 220°

Acetyl derivative C,H10(OAc), (above Oil, readily saponified

Bensoyl derivative C.H. (OBz). [128] Laminæ, sol alcohol and ether (Meyer, C B 59, 444)

Di oxy-pentane

CH, CH(OH) CH, CH(OH) CH, (177°). Formed by reducing methylene-di-methyl-diketone (acetyl acetone) with sodium amalgam (Combes, A Ch. [6] 12, 229). Liquid, sol water

Tri-oxy-pentane CHMe(OH) CH, CH(OH) CH, (OH) (180° at 27 mm) S G § 1 135, § 1 120 Got by oxidising CH, CH CH, CHMe(OH) with KMnO, The yield is 82 p c (Wagner, B 21, 3351) Syrup not volatile with steam

Tri-acetyl derivative C, H, (OAc), (270°)

at 740 mm SG 31 120, 20 1 101

Trı oxy-pentane CHEt(OH) CH(OH) CH₂(OH) (192° at 63 mm) Made 1 0851 bу oxidising CHEt(OH) CH CH₂ (114°) with KMnO, (Wagner, B 21, 3349) The yield is 63 pc Thick, sweet syrup, miscible with water, alcohol, and

Tri-acetyl derivative (265°) SG &

1 122, 18 1 103 Smells like onions Tri oxy-pentane

OHMe(OH) CMe(OH) CH₂(OH) 'Pentenyl glycerin' (158° at 24 mm)' Formed from tiglic alcohol by addition of bromine and subsequent distillation (Lueben a Zeisel, M 7, 68)

Tri acetyl derivative (149° at 18 mm)
Tetra-oxy pentane C₂H₁₂O₄ [253°] S 6 at 15° Formed by the action of lime on a solution of formic and acetic aldehydes (Tollens a Wigand, ▲ 265,316) Prisms Inactive to light HI and P form C_bH_sI_s(OH)_s [180°] and C_bH_sI_s(OH) [62°] Tetra-acetyl derivative [84°]

Penta-oxy pentane

{CH₂(OH) CH(OH)}₂CH(OH) [102°] Formed by reducing arabinose with sodium amalgam, the liquid being kept neutral with H2SO. Prisms or needles, v e (Kılıanı, B 20, 1233) sol water, v si sol cold alcohol

OXY-PENTANE TRICARBOXYLIC C,H,(OH) C(CO,H), CH,CO,H Formed from C,H, C(CO,H), OH,CO,H by successive treatment with HBr and KOH (Hjelt, B 16, 1258)

Anhydride C, H10O, Dicarbocaprolactonic acid [153°] Triclinic crystals (from water) .-BaC.H.O. —Ag.C.H.O. pulverulent pp OXY-PENTANE PHOSPHONIC ACID

C.H. CH(OH).PO(OH)₂ [184°] Formed from isovaleric aldehyde and PCl, followed by water (Fossek, M 5, 627, 7, 20) Monoclinic scales Yields isovaleric aldehyde on distillation and on treatment with KMnO, PCl, forms C, H10Cl POCl2 (134°-140° at 22 mm) Reduced by HI and P to isopentane phosphonic acid C₅H₁₅PO₃ [161^o]
—BaA"²aq —Ba(HA"), —Ag₂A" amorphouspp
OXY-PENTANE SULPHONIC ACID

C_sH₁₀(OH)SO_sH Amylene isethionic acid Formed from chloro amyl alcohol (amylene chlorhydrin) and Na₂SO₃ (Falk, J pr [2] 2,272) Decomposed on evaporation of its solution— NaA' -CaA'2 -CuA'22aq pale blue laminæ

An isomeric acid is formed by the action of 80, on isoamyl alcohol (Schwarz, B 3, 691) -

crystalline

OXYPENTIC ACID C,H,O, aq or C,H,O, [198°] Formed from ethyl acetoacetic ether, bromine, and alcoholic potash (Demarcay, C R 88, 289) Crystals, m sol cold water monia converts its ether into a substance [77°],

and its chloride into another body [204°] Zn and H₂SO₄ yield C₂H₁₀O₄ [95°] Oxypentic acid is perhaps $\Delta^{\mu}\gamma$ hydromuconic acid (Gorboff, J B.

OXYPENTINOIC ACID C.H.O. 2 e

Aceto-acrylic acid. OH, CO OH CH CO2H [125°] Prepared by boiling an aqueous solution sodium \$\beta\$ bromo-lævulate for a few minutes, neutralising with Na2CO3, again boiling, neutralising again, and so on till the solution finally remains alkaline after boiling (Wolff, B 20, 426) Glistening plates V sol alcohol and ether, less sol cold water and chloroform

Salts —CaA'2 —ZnA'2 amorphous —AgA' needles

OXY-PHENANTHRAQUINONE v PHENAN-THRAQUINONE

DIOXY-PHENAZINE C12H8N2O2 Formed by heating di-amido phenazine with conc HClAq at 200° (Fischer a Hepp, B 23, 843, Nietzki a Hasterlik, 24, 1337) Reddish yellow needles (containing jaq) —B'2H2SO, 2aq

Di-acetyl derivative [230°] (F a H), [226°] (N a H) Pale yellow tables

Dioxytriphenazine

NHCCOCN C,H, C,H, Quinone homo. ∨и ссосин∕

fluorindin Formed by heating dio nitro diphenyl quinone with alcoholic ammonium sul phide at 100°, the product being oxidised by exposure to air (Leicester, B 23, 2794) green crystals, yielding a violet powder solution in HOAc exhibits brownish red fluor

OXYDIPHENYLS All these compounds yield diphenyl when distilled with zinc dust

p Oxy diphenyl C₆H₅ C₆H₄ OH [165] 307°) Formed by fusing diphenyl sulphonic acid with potash (Latschinoff, B 6, 194, Osten, B 7, 170), by warming diazobenzene chloride with phenol, and in small quantity in the decom position of diazobenzene chloride by water Plates, volatile with (Hirsch, B 23, 3705) steam Yields a mono nitro derivative [67°] and a di nitro derivative [154°]

Acetyl derivative [89°] Plat alcohol and ether (Kaiser, A 257, 101) Plates, v sol

 $[152^{\circ}]$ Tables Bensoyl derivative An isomeric or identical oxydiphenyl [152°] is obtained from p amido diphenyl by the diazo reaction (Hubner, A 209, 348)

00 Di-oxy-diphenyl C₆H₄(OH) C₆H₄(OH) [99°] Formed by potash fusion from diphenyl disulphonic acid (Limpricht, A 261, 331), and by dropping fluorene into fused KOH at 400° (Hodgkinson a Matthews, C J 43, 168) Crys tals (from benzene ligroïn)

pp D1-oxy-diphenyl [272°] (above 360°) Formed from benzidine by the diazo reaction (Griess, J 1866, 461, Hirsch, B 22, 336), and by potash fusion from diphenyl di-p sulphonic acid (Engelhardt a Latschinoff, Z 1871, 261, Doebner, B 9, 180) Got also by distilling dioxy-phenyl benzoic acid with lime (Schmidt a Schultz, A 207, 334, B 12, 490) Obtained also by passing a rapidly alternating electric current through a solution of phenol (Drechsel, J. pr [2] 29, 237) Laminæ (from alcohol)

Di-acetyl derivative [160°] Ethyl ether [176°] (Hirsch)

on-Di oxy-diphenyl [161°] (342°) Formed | in small quantity by potash fusion from phenol o- and p- sulphonic acids (Lincke, J pr [2] 8, 43, Herzig, B 15, 2234), and by the action of nitrois acid on op di amido diphenyl (Schmidt, A 207, 357, B 12, 497) Yields a di acetyl derivative [94°]

By fusing phenol with potash two more di oxy diphenyls [123°] and [190°] have been obtained (Barth a Schreder, A 156, 93, B 11, 1336) The one melting at 123° yields

Tri oxy-diphenyl C₈H₄(OH) C₈H₄(OH)₂ Two isomerides of this formula [180°] and [205°] are formed by fusing fluorene sulphonic acid with potash at a little above 400° (Hodgkinson a Matthews, C J 43, 167) Neither gives any colour with FeCl, The compound [180°] forms an acetyl derivative [100°]

Tetra oxy diphenyl $C_6H_3(OH)_2C_6H_3(OH)_2$ Dipyrocatechin [84°] Formed from diphenyl (a) disulphonic acid by potash fusion (Barth, B 11, 1336) Needles FeCl, colours its solution

Tetra oxy diphenyl C12H10O4 Diresorcin [310°] Formed in small quantity by fusing resorcin or phenol with NaOH (Barth, B 12, 503, Benedikt, M 1, 355, 5, 177, Herzig, M 11, 419) Needles (containing 2aq) Gives a blue colour with FeCl, Phthalic anhydride and H₂SO, at 120° form C₂,H₂₀O₂ 4aq, which gives blue solutions with alkalis

[159°1 Acetyl derivative C12Hc(OAc), Benzoyl derivative C, H, (OBz), [199°] Formed from phloroglucin, BzCl, and NaOH

(Skraup, M 10, 721, Pukall, B 20, 1148)

Ethyl ether C, H₆(OEt), [1149] Plates

Tetra oxy-diphenyl C₆H₅(OH)₂C₆H₅(OH)₂

Dihydroquinone (237°) Formed by fusing hydroquinone with NaOH (Barth, M 5, 600) Plates Tastes sweet FeCl, colours it red, and then forms diquinhydrone C12H8O4 and diquinone C₁₂H₆O₄ [187°

Hexa-oxy diphenyl $C_6H_2(OH)_3$ C_6H (OH)Formed by heating hydrocœrulignone with HClAq at 200° (Liebermann, A 169, 239, B 9, 1887) Plates, m sol water FeCl, gives a bluish grey pp Iodine yields C12H3O6, crystal-

lising in blue needles

Tri methyl ether $C_{12}H_4(OMe)_3(OH)_3$ Formed from corrulignone and H2SO, (Fischer,

B 8, 158)

Tetra methyl ether C₁₂H₄(OMe)₄(OH)₂ Hydrocærulignone [190°] Formed by reduc tion of cærulignone (Liebermann, A 169, 226) Monoclinic prisms (from alcohol) FeCl, oxidises it to corulignone Yields

C₁₂H₄(OMe)₄(OAc)₂[217°-225°] -Na₂C₁₆H₁₆O₆-KA" 4aq (Ewald, B 11, 1623)

Hexa-methyl ether C12H4(OMe) [126°] C12H4(OH)2(OEt) Tetra-ethyl ether [176°] Crystals (from alcohol) (Hofmann, B 11, 802)

Hexa-acetyl derivative C,H (OAc)

Hexa-propionyl derivative Needles Di - bromo hexa - oxy - diphenyl Tetra derivative C₁₂H₄Br₂(OH)₂(OMe)₄ Formed from C₁₂H₂Br₂(OAc)₂(OMe)₄ methyl derivative [178°], which is got from di acetyl corulignone, acetic acid (Salkowski, B 12, 1438), and by

HOAc, and bromine (Hayduck, B 9, 929) yields C₁₂H₂Br₂(OMe), [140°]

References - DI BROMO and DI CHLORO-HEXA OXY DIPHENYL

(β) Hexa oxy diphenyl Formed by fusing ellagic acid with potash (Barth a Goldschmidt, B 12, 1244) Needles, blackening at 250°, and melting at a higher temperature. Its alkaline solution is blue, changing in air to red

(γ) Hexa-oxy-diphenyl Formed from ellagic acid by fusion with NaOH (B a G), or by treatment with sodium amalgam (Cobenzl, M 1, 672) Needles, blackening at 230° Its alkaline

solution is red, changing in air to green

 (δ) Hexa oxy diphenyl Formed by fusing hydroquinone with NaOH (Barth a Schreder, M 5, 597) Plates, blackening and melting near 290° Its alkaline solution is red

Acetyl derivative [172°] OXY PHENYL ACETAMIDINE Needles C₈H₁₀N₂O Formed 16 CHPh(OH) C(NH)(NH2) [110°] from mandelic imido ether and alcoholic NH, (Beyer, J pr [2] 28, 191) Needles (from ether) —B'HCl [214°] Prisms (from water)

Di acetyl derivative

CHPh(OAc) C(NH) NHAc [210°] (Pinner, B 23, 2948)

OXY-PHENYL ACETAMIDOXIM

C_sH_s CH(OH) C(NH_s)(NOH) [159°] from the nitrile of mandelic acid and alcoholic hydroxylamine (Tiemann, B 17, 126, Gross, B 18, 1074) Crystals (from alcohol) Yields the 18, 1074) Crystals (from alcohol) Yields the derivatives $C_aH_aNaN O_2$, B'HCl, $C_aH_aEtN_2O_2$ [89°], and $C_aH_a(CH_2Ph)N_aO_2$ [103°]

Reactions —1 COCL, forms the compound (CHPh(OH) C(NH₂) NO)₂CO [121°] —2 Its by

drochloride reacts with potassium cyanate, forming CHPh(OH) C(NOH) NH CO NH₂ [127°] — 3 Phenyl cyanate forms the CHPh(OH) C(NOH) NH CO NHPh the compound [155°] -ClCO₂Et yields CHPh(OH) C(NH₂) NOCO₂Et [107°]

Acetyl derivative CHPh(OH) C(NH.) NOAc [140°] Crystals (from alcohol)

Di acetyl derivative [113°] Benzoyl derivative C15H14N2O3 Acetyl benzoyl derivative [165°] o OXY PHENYL-ACETIC ACID

[21]C₆H₄(OH) CH CO₂H [137°] Formed from o oxy phenyl-glyoxylic acid by reduction with sodium amalgam to C.H. (OH) CH(OH) CO.H., and further reduction of this acid with HI (Baeyer a Fritsch, B 17, 975) Needles, v sol water Gives a violet colour with FeCl, On heating it yields the lactone

 $C_eH_4 < CH_2 > CO$, crystallising in tables [49°]

(237°)

m Oxy phenyl-acetic acid [129°] Formed by saponification of its nitrile and from mamido-phenyl acetic acid by the diazo reaction (H Salkowski, B 17, 507) Needles, v sol water Coloured violet by FeCl

[3 1]C₆H₄(OH) CH₂ CN Nitrile Formed from C₆H₁(NH) CH₂ CN and nitrous Trimetric tables, v sol alcohol and hot acid

water

p-Oxy phenyl acetic acid [148°] by the action of nitrous acid on p amido phenylsaponifying its nitrile, which is a product of the action of AgNO, on sinalbin (Will a Lauben heimer, A 199, 156, Salkowski, B 22, 2137) Occurs in human urine (Baumann, B 13, 280) Prismatic needles, sol water and alcohol FeCl, gives a dark colouration —NH,A' —CaA', 4aq -PbA'₂—AgA' minute needles
Methyl ether C₆H

Methyl ether C.H. (OH) CH2 CO Me (310° 1 V) S G 2 1 1948, 2 1 1786 Oil Ethyl ether EtA' (314° 1 V) S G 2

1 1886, 18 5 1 1226

Netrile [70°] (330 5° 1 V) Made like 18m isomeride (Salkowski, B 22, 2137) Triclinic crystals Yield's C₆H₄(OMe) CH₂CN (287° 1 V) 8 G 2 1 1001

Methyl derivative CaH4(OMe) CH2 CO3H [86°] Formed from C.H. (OMe) CH2Cl and KCy, the product being saponified (Cannizzaro, A 117, 243) Pearly plates —AgA'

Ethyl derivative [88°] Plates Amide C.H. (OH) CH2 CONH2 [175°] Methyl derivative of the amide C₆H₄(OMe) CH₂ CONH₂ [189°] Scales

a Oxy phenyl acetic acid v Mandelic acid

ao-Di oxy-phenyl acetic acid C₆H₄(OH) CH(OH) CO_.H Formed from salicylic aldehyde, HCy, and HCl (Ploschl, B 14, 1317), and also by reducing oxy phenyl glyoxylic acid (Bayer a Fritsch, B 17, 974) Yields a crystalline anhydride

Methyl derivative of the nitrile C_eH₄(OMe) CH(OH) CN [71°] Formed from methyl salicylic aldehyde and HCy (Voswinckel,

B 15, 2025) Colourless crystals

Di-oxy phenyl-acetic acid [1 3 5]C₆H₃(OH)₂ CH₂ CO₂H [54°] Formed from C_6 H(OH)₂(CO₂Et)₂CH₂CO₂Et and alcoholic

potash (Pechmann, B 19,1449) Crystals (containing aq) —PbA'₂ 2aq needles (from water) ap-Di oxy phenyl-acetic acid Methyl de-C₆H₄(OMe) CH(OH) CO₂H rivative Formed from anisic aldehyde, HCy, and HCl

(Tiemann a Kohler, B 14, 1976) Needles—CaA'₂—AgA' amorphous pp

Amide C₂H₄(OMe) CH(OH) CONH₂ [159°]

Nitrile C₂H₄(OMe) CH(OH) CN [63°]

Di oxy-phenyl acetic acid

 $C_6H_3(OH)_2 CH_2 CO_2H [4 3 1]$ **Homoprotocate** churc acid [127°] Formed by heating its methyl derivative with HClAq at 175° (Tiemann a Nagai, B 10, 207) Slender needles (from benzene) FeCl₃ gives a green colour

Di acetyl derivative

C_eH₃(OAc)₂ CH₂ CO₂H [90°] (Nagai, B 11,658) Methyl derivative

C₆H₃(OMe)(OH) CH₂ CO₂H [3 4 1] Homovanillic acid [143°] Made from its acetyl derivative [140°], which is got by oxidising acetyl eugenol Di-methyl derivative C_cH₃(OMe)₂.CH₂.CO₂H Homoveratric acid [99°]

(Tiemann a Matsmoto, B 11, 143) Needles

(containing aq)

Methylene derivative C₆H₂(O₂CH₂) CH₂ CO₂H [128°] Got from safrol, KMnO₄, and dilute HOAc (Tiemann, B 24, 2882) Yields MeA' (279°), EtA' (291°), and an amide

A di-oxy phenyl-acetic acid [168°] occurs in urine after poisoning by phosphorus (Baumann, H 6, 192) It crystallises in small needles

Tri-oxy phenyl-acetic acid, Methylene derivative [4 3 1]C₆H₈(O₂CH₂) CH(OH) CO H [153°] Made from piperonal by treatment with HCy and saponification (Lorenz, B 14, 793)

Hexa-oxy-d1-phenyl acetic acid methyl derivative (C₆H₂(OMe)₃)₂C(OH) CO₂H [175°] Formed by boiling the hexa methyl derivative of hexa oxybenzil with potash (Marx, A 263, 255)

v sol alcohol, sl sol water a-Oxy-di-phenyl-acetic acid v Benzilic Acid Tri-oxy-di-phenyl-acetic acid derivative v AnisiLic acid

(B 2) OXY (A) PHENYL-ACRIDINE

 $C_6H_4 < N > C_6H_3(OH)$ [c 275°-280°] Formed by heating p oxy di-phenylamine with benzoic acid and $ZnCl_2$ Formed also by heating (B 2)amido (A) phenyl acridine with HCl at 200°-220° (Hess a Bernthsen, B 18, 695) Thin yellow crystals V sol alcohol and acetic acid. less sol ether Dissolves in caustic alkalis and The ethereal and alcoholic solutions in acids have a slight bluish-violet fluorescence The salts are all rather sparingly soluble, and have a tendency to separate in a gelatinous form

Acetyl derivative C,9H,3N(OAc) [174°], glistening four sided prisms

OXY - PHENYL - ACRYLIC ACID v OXY CINNAMIC ACID and COUMARIC ACID

Oxy-di-phenyl-acrylic acid Methyl deri vative C.H. (OMe) CH CPh CO2H [189°] Made from anisic aldehyde, sodium phenyl acetate, and Ac,O at 160° (Oglialoro, G 9, 533) Prisms, yielding C.H. (OMe) CH CHPh when heated

Methyl derivative of the nitrile C_cH₄(OMe) CH CPh CN [93°] Formed from anisic aldehyde, benzyl cyanide, and alcoholic NaOEt (Frost, A 250, 159) White needles

Reference -PHENYL COUMARIN

TRI OXY-PHENYL ALLYL KETONE cording to Schiff (A 253, 336), filicic acid (vol 11 p 548) is the isobutyryl derivative of this ketone $[5\ 3\ 1\ 2]\ C_6H_2(OH)_2(O\ COPr)\ CO\ C_8H_5$

OXY TRI PHENYL-ALLYL-PYRROLE

 $N(C_3H_3)$ < $CPh CH CPh_2 CO CPh_2 CPh_2 CO CPh_2 CO CPh_2 CO CPh_2 CO CPh_2 CO CO CPh_2 CPH_2 CO CPH_2 CO CPH_2 CP$ [112°] Formed by heat ing anhydracetophenone - benzil PhCBz CHBz

with alcoholic allylamine at 100° (Japp a Klingemann, $C J \tilde{5}7, 707$ Monoclinic prisms (from alcohol), a b c = 166511844, $\beta = 88^{\circ}53'$

o OXY PHENYL-ALLYL THIO UREA C₆H₄(OH) NH CS NHC₃H₃ [99°] Formed from o amido phenol and allyl thiocarbimide in alcoholic solution (Von Chelmicki, J pr [2] 42, 442) V sl sol cold, v sol hot, water

o OXY PHENYL AMIDO ACETIC ACID C₆H₄(OH) CH₂ CO₂H Oxy - phenyl - glycocoll Formed by boiling chloro acetic acid (1 mol) with o amido phenol (2 mols) and water (Vater, J pr [2] 29, 289) Plates (containing aq), sl sol water, v sol alcohol FeCl, colours its solutions red At 105° it yields an anhydride which crystallises from alcohol in cubes

Methyl derivative C₆H₄(OMe) NH CH₄.CO₂H [142°] Formed from o anisidine and chloro acetic acid Rectangular plates -PbH2A' -B'HCl crystals

Ethyl derivative C.H. (OEt) NH CH, CO.H. Formed from chloro acetic acid and CaH4(OEt)NH2 -- EtA' long waxy needles -- | violet needles (from alcohol), forming a violet EtA/HCl

p-Oxy-phonyl amido-acetic acid

C₈H₄(OH) NH CH *CO₂H Formed from chloroacetic acid and p amido phenol (V) Plates, sl sol water and alcohol FeCl₃ colours its solu tions red -NaA'

Methyl derivative

C_aH₄(OMe) NH CH₂ CO₂H Formed ın lıke manner from p anisidine (V), and also by sa ponifying its nitrile, which is got by heating anisaldehyde cyanhydrin with alcoholic NH₃ (Tiemann a Kohler, B 14, 1976)—Needles, sol hot water CuA'2 -HA'HCl

Ethyl derivative

C₆H₄(OEt) NH CH₂ CO₂H [163°] Crystals (con Yields, on heating taining xaq) C.H. (OEt) NH CH, CO NHC, H. (OEt) [140°] and other bodies (Bischoff a Nastvogel, B 22, 1788)

O-OXY-PHENYL-AMIDO-BENZENE SUL-PHÔNIC ACID C₀H₃(OH)(NHPh) SO₄H Formed from C₈H₄(OH)NHPh [1 4] and cone H₂SO₄ at 100° (Limpricht, B 22, 2910) Small grey prisms Does not melt below 260°

OXY-PHENYL AMIDO CROTONIC ETHER Methyl derivative C13H17NO2 [46°] Formed from p anisidine and acetoacetic ether (Conrad a Limpach, B 21, 1649)

DI OXY-PHENYLAMIDOETHYL BENZOIC Methylene derivative of the anhydride C16H13NO, 1e

 $CH_2 < 0 > C_0H_2 < CO NPh CH_2 CH_2 CH_2 CH_2$ [157°] Formed from CH2O, CeH2(C2H4Cl) CO2Me and alcoholic aniline (Perkin, jun, C J 57, 1036) Prisms, v sl sol hot alcohol

OXY PHENYL AMIDO NAPHTHOQUINONE C10H4O2(OH)(NHPh) Oxy naphthoquinone aniland boiling KOHAq (Plagemann, B 16, 896) Formed from C₁₀H₄ClO₂(NPh NO) Deep blue needles with metallic lustre, sol alkalıs

O OXY-PHENYLAMIDO PHENYL-ACETO NITRILE Methyl derivative

C.H. (OMe) CH(NHPh) CN [61°] Formed by the action of aniline on C.H. (OMe) CH(OH) CN (Voswinckel, B 15, 2027) Six sided tables, sol alcohol

OXY PHENYL AMIDO QUINONE ANILIDE CaH2(OH)(NHPh)O(NPh) Formed by heating its others with alcoholic potash (Zincke a Hagen, B 18,788) Small scales, sl sol alcohol Cold, very dilute potash, converts it into the quinone C.H.2(OH)(NHPh)O2, a blue crystalline pp de composing above 200°

Methyl ether CeH2(OMe)(NHPh)

[194°] Formed by warming the compound C₈H₂(NHPh) O(NPh) with MeOH and H₂SO₄ (Z a H), and also from azophenine, MeOH, and H₂SO₄ (Fischer a Hepp, B 21, 677, A 262, Brownish red plates, forming blue salts

with acids, C.H. (OMe) (NHPh)O, [189]

Ethyl ether C.H. (OEt) (NHPh)O (NPh).

[137] Formed in like manner, using EtOH

Isobutyl ether [138°] Needles OXY-PHENYL-AMIDO-THYMOQUINONE

C_sMe(C_sH_s)(OH)(NHPh)O₂ [135°] Formed by boiling oxy thymoquinone with aniline and aleohol (Schulz, B 16, 902). Lustrous, dark-

solution in NH,Aq

OXY-PHENYL AMIDO-TOLUQUINONE

C₆HMeO₂(OH)(NHPh) Formed from di phenyl di amido toluquinone by boiling with alcoholic H₂SO₄ (Hagen a Zincke, B 16, 1560) Deep blue needles (from alcohol), decomposing at 250°

Anilide C₆HMe(OH)(NHPh)<0 NPh

Formed by treating its ethers with acids or Brown needles (from HOAc) and C, H, MeN, O, [131°], C, H, StN, O, [116°] and C, H, (C, H,)N, O, [117°] are crystalline ω OXY-PHENYL-ω-AMIDO-TOLYL GLYCOL-

LIC ACID NHPh CH(OH) CaH, O CH2 CO2H Formed from o aldehydo phenoxy acetic acid and aniline (Rossing B 17, 2992) Very un-[191°] stable in alkaline solution — HA'HCl HA'H₂SO, [186°] Yellow needles, v sol hot water

m OXY DIPHENYLAMINE

C_cH₃NH C_cH₄(OH) Phenyl anudo phenol [82°] (c 340°) Formed by heating resorcin (1 mol) with aniline (4 mols) and CaCl₂ (2 mols) for eight hours at 280°, the yield being 85 p.c. of the theoretical (Calm, B 16, 2786, Kohler, White pearly plates, v sol **B** 21, 908) Yields a crystalline nitrosamine alcohol NPh(NO) C₄H₄OH [115°]—HA'HCl needles H₂A₂H₄SO₄ needles—BaA'₂5aq colourle plates, sol water colourless

p Oxy diphenylamine C.H.NH C.H.OH [70°] (330°) Prepared by heating hydroquinone (1 mol) with aniline (4 mols) and CaCl₂ (2 mols) for ten hours at 260°, the yield being 90 pc (Calm, B 16, 2799, 17, 2431) Formed also by heating hydroquinone with aniline for sixteen hours at 300° (the yield being 85 pc), and by the action of aniline on quinone phenylimide (Bandrowski, M 9, 133, 416) Plates, v sol aqueous alkalis and acids, sl solwater Yields a nitrosamine [95°] On oxida tion with HgO in benzene it yields C12H2NO [97°] (B) —HA'HCl slender needles, decomposed by water -HA'HBr needles

Isobutyl ether C,H,A' $[68^{\circ}]$

Formyl derivative C, H, NO(CHO) [178°] White needles, sol alcohol

Di acetyl derivative NPhAc C.H.OAc

[120°] Monoclinic prisms Di-benzoyl derivative [175°] Prisms

Di oxy-diphenylamine NH(C6H4OH)2 Formed by heating resorcin with ammoniacal CaCl at 200° (Seyevitch, C R 109, 946). Minute crystals (from dilute alcohol)

O OXY PHENYL-ANGELIC ACID

C₁₁H₁₂O₃ 1 e C₆H₄(OH) CH CMe CH₂ CO₂H?
[73°] Formed from salicylic aldehyde, sodium pyrotartrate, and Ac₂O (Fittig a Brown, A 255, 290) Large plates, v sol BaA', 4aq — AgA' flocculent pp chloroform --

o-Oxy-phenyl-angelic acid C₆H₄(OH) CH CEt CO₂H [174°] Formed by boiling its anhydride with potash (Perkin, A 150, 84, C J 21, 472) Flat prisms (from dilute alcohol), sl sol water and chloroform. AgA' yellowish pp

Anhydrids C.H. CH CEt. [71°] (299°). Formed by boiling sodium salicylic aldehyde with butyric anhydride (Perkin, A 147, 233, C J 21, 53, 472, Fletcher, C J 39, 447) Formed also by distilling coumaryl propionic acid (Fittig, A 255, 288) Mor abc=1 192 1 694, β=67° 18' Monoclinic crystals,

(a) Methyl derivative C.H. (OMe) CH CHEt CO.H [88°] Formed from the anhydride NaOH, and MeI, the resulting $C_0H_4(OMe)$ CH CHEt CO_2Me (282°) being saponified (Perkin, C J 39, 435). Monoclinic

crystals

(B) Methyl derivative C.H. (OMe) CH CEt CO₂H [105°] Formed from methyl-salicylic aldehyde, butyric anhydride, and sodium butyrate Needles (from alcohol) Yields CaH2Br2(OMe) C4H6Br2 CO2H [159°] and C.H. (OMe) CH CEt CO2Me (292°) HI forms a compound whence Na₂CO₂ produces o butenylphenol

p-0xy-phenyl-angelic acid $C_0H_4(OH)$ CH CEt CO_2H

Methyl derivative [124°] Formed from anisic aldehyde, butyric anhydride, and sodium butyrate (Perkin) Needles (from alcohol)

γ Oxy-phenyl-angelic acid Anhydride C.H.CHCCHCMe [53°] Made by distilling a phenyl levulic acid (Erdmann, A 254, 219) Plates (from CS, and ligroin)

Di oxy-phenyl-angelic acid Methylene

derivative

CH₂ CO₂ C₆H₃ CH₂ CH CH CH₂ CO₂H Hydropiperic acid [78°] Formed by reducing piperic acid with sodium amalgam (Foster, A 124, 117, Buri, A 216, 172, Weinstein, A 227, 32) Needles (from hot water) Changes on heating with NaOHAq into a less soluble isomeric acid [131°] Both acids combine with bromine—NH₄A'—KHA₂—BaA'₂—AgA' crystalline pp

Di-oxy-phenyl angelic acid Methylene derivative CH2 CO C.H, C.H. CO2H 160°] Prepared by heating piperonal with butyric anhydride and NaOAc (Lorenz, B 14, 786) Long felted needles (from dilute alcohol),

sl sol water -AgA'. curdy pp Di p-oxy di-phenyl angelic methyl derivative C,H,(OMe) CH CH CH (CO,H) CH, C,H,(OMe) [111°] Made by reducing acid Dı.

(C,H,(OMe) CH),C,H CO,H with sodium amal gam (Fitting a Politis, A 255, 302) Hard needles (from CS₂), sl sol water, v sol alcohol Yields a dibromide C₁₉H₂₀Br₂O₄—CaA'₂2aq— AgA' flocculent pp

DI-OXY-DI-PHENYL-ANTETRAZINE DI-HYDRIDE N = O(OH) C CH, C — N CPh OPh N — C CH, C C(OH) N

Formed from dioxyterephthalic ether, benzamidine hydrochloride, and dilute (10 p c) NaOHAq (Pinner, B 22, 2624) Crystalline powder, insol water and alcohol—C₂₂H₁₄Na₂N₄O₂4aq white needles

OXY-PHENYL-ANTHRANOL CaH14O2 16 $C_eH_4 < C(O_eH_4OH) > C_eH_4$ Formed by the action of H.SO, on oxy-triphenyl-methane carboxylic acid (Pechmann, B 13, 1616) Exhibits green fluorescence in ethereal solution.

Di-oxy-phenyl-anthranol CaHLO. C_eH_4 $C(O_H^4,O_H^2)$ C_eH_4 Phenolphthalidin A sticky mass got by dissolving phenol phthalin in H₂SO₄ and pouring into water (Baeyer, A. 202, 91) Its ethereal solution fluoresces green Water at 170° converts it into phenol phthalia Potash-fusion gives di oxy benzophenone

OXY-PHENYL-ARSINE v Arsine

DI-OXY-PHENYL-TRIAZOLE CaH, No O2 1 e C₆H₅ N—C(OH) N or C.H. N CO N = C(OH)urazol [263°]

Formation -1 By heating phenyl hydrazine hydrochloride (1 pt) with urea (2 pts) for 4 or 5 hours at 160°, the yield is 70-80 pc of the hydrazine hydrochloride used -2 By heating phenyl semicarbazide (1 pt) with urea (2 pts) for 4 hours at about 160°

Properties - Colourless glistening plates M sol hot water, sl sol cold water, v sol hot alcohol, sl sol ether Dissolves in cold aqueous alkalis and ammonia, and is reppd by acids unaltered It does not reduce alkaline solutions of Ag or Cu It is not affected by boiling with alkalıs or acıds (Pınner, B 20, 2358)

TETRA-OXY-PHENYL-BENZOPYRAZOLE

 $\begin{array}{c} NPh < \stackrel{CO}{\sim} \stackrel{C}{\sim} \stackrel{C(OH)}{\sim} \stackrel{C=N}{\sim} NPh \end{array}$ [c 150°] Formed by the action of HClAq on the phenylhydrazide which is made by warming di oxy quinone dicarboxylic ether with alcohol and phenyl hydrazine (Böniger, B 22, 1291) Begins to decompose at 125°—(NH₄) A" ochre yellow powder, sol water

OXY-DI-PHENYL-BENZYLIDENE PYR-AZOLE NPh CO CHPh [147°] Formed from oxy di phenyl pyrazole and benzoic aldehyde (Knorr a Klotz, B 20, 2548) Needles

Di oxy-tetra phenyl benzylidene dipyrazole $\binom{\text{NPh CO}}{\text{N} = \text{CPh}}$ CH)₂ CHPh [c 220°] Formed from benzoic aldehyde and excess of oxy-di phenyl pyrazole

Exo OXY PHENYL-BENZYL KETONE BENZOIN

Tri oxy-phenyl-benzyl ketone Di-methylderivative v Anisoin

Hexa oxy-phenyl-benzyl-ketone methyl derivative C_sH₂(OMe), CO CH₂O_sH₂(OMe), [162°] Formed from hexamethoxy benzil, HOAc, and zinc dust (Marx, A 263, 255) Needles, insol cold water

OXY-PHENYL-BENZYL-METHYL PYRIM- $\begin{array}{ccc} \textbf{IDINE} & \textbf{CPh} \textcolor{red}{\leqslant_N^N} \overset{\textbf{OMe}}{\textbf{O(OH)}} \textcolor{blue}{>} \textbf{O CH_Ph} \end{array}$ Formed from benzamidine hydrochloride, benzylacetoacetic ether, and dilute (10 pc) NaOHAq (Pinner, B 22, 1626) Needles, insol water, v

sl sol alcohol D1 oxy-phenyl-bensyl-methyl-pyrimidine Ethyl derevative

 $C_eH_4(OEt)$ C < N C(OH) C(OH) [242°] Formed p-ethoxy-benzamidine hydrochloride, benzyl-acetoacetic ether, and NaOHAq (Pinner, B 23, 2955). Needles, ▼ sl. sol. hot alcohol

OXY-PHENYL BENZYL-PYRIMIDINE

 CH_2Ph $C < N CPh \ C(OH) > CH$ [233°] Made from phenylacetamidine hydrochloride, benzyl acetoacetic ether and dilute (10 pc) NaOHAq (Pinner, B 22, 1623) Needles, v sl sol water Oxy-phenyl di-benzyl pyrimidine

 $CH_2Ph C \stackrel{N C(CH_2Ph)}{\sim} CPh [180^\circ]$ Formed by heating 'cyanbenzyline' (derived from benzyl cyanide) with HClAq (Wache, J pr [2] 39, 258)

Di oxy phenyl benzyl pyrimidine

CHPh(OH) C N CPh CHPh(OH) CH [218°] Formed from a oxy phenyl acetamidine and benzoylacetic ether (Pinner, B 23, 2951) Felted needles, v sl sol water, sol alkalıs and acıds

ν OXY PHENYL BIURET

(NHPh CO)₂N(OH), [178°] Formed by the action of an aqueous solution of hydroxylamine on phenyl cyanate (von der Kall, A 263, 263) Needles, sl sol hot water Does not reduce Fehling's solution

p-OXY PHENYL-BROMO p-TOLYL THIO-UREA C₆H₄(OH) NH CS NH C,H₆Br

Acetyl derivative [156°] Formed by the action of acetyl oxy phenyl thiocarbinide on bromo-p toluidine (Kalckhoff, B 16, 1832) V sol acetic acid, sl sol alcohol and ether, insol

OXY PHENYL BUTANE v BUTYL PHENOL

Dı oxy phenyl butane

CHPh(OH) C,H, CH OH (c 200°) A thick syrup formed by reduction of C₆H₅ CO C₂H₄ CHO (Burcker, A Ch [5] 26, 469)

Di oxy di phenyl butane

[120°] Formed by CPh Me(OH) CPh Me(OH) adding sodium amalgam to a solution of acetophenone in dilute alcohol (Emmerling a Engler, B 4, 147, 6, 1005, Buchka, B 10, 1714) Long prisms, insol water, v sol alcohol Split up by long boiling in acetophenone and phenyl methyl carbinol (Zincke a Thorner, B 13, 641)

Di oxy tetra phenyl butane CH.Ph CPh(OH) CPh(OH) CH2Ph [213°] Formed, together with an isomeride [172°], by reducing benzoin with zinc (Limpricht a Schwanert, A 155, 60, Zagoumenny, B 7 1651, Wislicenus, A 248, 5) The compound [213°] is formed, together with an isomeride (?) [61°], by reducing benzoin with Na and alcohol (Limpricht, A 155, 98) The compounds [172°] and [213°] are both converted by heat into phenyl benzyl ketone and phenyl benzyl carbinol

OXY-DI PHENYL-BUTANE CARBOXYLIC C₆H₅ CH(CO₂H) CH₂ CH(OH) CH₂·C₆H₅ Tetrahydrocornicularic acid Formed by re ducing hydro cornicularic acid with sodium amalgam (Spiegel, A 219, 35) Thick oil, decomposed by boiling with water, yielding the lactone Lactone C, H, O, [71°]

Oxy phenyl butane dicarboxylic acid v. Oxy-

BENZYL-PYROTARTARIC ACID

Di-oxy-di-phenyl-butane dicarboxylic acid C.H.(OH) CH, CH(CO.H) CH(CO.H) CH, C.H.OH Formed by heating salicylic aldehyde with sodium succinate and Ac.O, saponifying the resulting 'dicoumarin,' and reducing the product with sodium amalgam (Fittig a Dyson, A

255, 281) Colourless crystals, v sol alcohol.— CaC₁₈H₁₆O₆ 6aq —Ag₂A" bulky white pp Lactone

C_sH_s $\stackrel{O}{\leftarrow}$ CH CH $\stackrel{CO}{\leftarrow}$ C_cH_s Dicoumarin tetrahydride [224°] Formed by heating the acid above 100° Needles (from chloro-

form alcohol) Di oxy-di phenyl butane dicarboxylic acid.

CH CH, CH, CH, Lactone C_eH₄CO `o o co

[210°] Formed by treating C₂H₄(CO C₆H₄ CO₅H)₂ with sodium amalgam (Gabriel a Michael B 10, 2209) Needles (from alcohol), insol water The corresponding acid is unstable

DI p-OXY-DI PHENYL BUTINENE

methyl ether C₆H₄(ŎMe) CH CH CH CH C₆H₄(OMe) A body formed on heating anisic aldehyde with sodium succinate and Ac2O at 120° (Fittig a. Politis, A 255, 307) Crystals, insol water, m. sol HOAc

DI-OXY-DI-PHENYL-BUTINENE DI. CARBOXYLIC LACTONE

C₆H₄<0-CO CO O O CH₄
C_H C CH C CH CH₄
Co CH C CH₅
Co CH₄
Co CH₄
Co CH₅
Co CH₄
Co CH₅
Co CH₄
Co CH₅
Co CH₅
Co CH₄
Co CH₅
Co C Dicoumarin hyde with sodium succinate and Ac20 at 140° (Fittig a Dyson, A 255, 275) Needles (from HOAc) Not attacked by cold alkalis

o oxy phenyl butylene dicarboxy.

LIC ACID Lactone C,H, CH CCHMe CO,H [171°] Made by heating salicylic aldehyde with sodium pyrotartrate and Ac2O for 30 hours at 120° (Fittig a Brown, A 255, 285) Plates (from water) Yields Ba(C1.H2O4)2 3aq, CaA'. 5aq, and AgA

Di oxy di phenyl butylene dicarboxylic acid Lactonic acid

by boiling dicoumarin with NaOHAq and adding sodium amalgam (Fittig a Dyson, A 255, 277) Needles, sl sol hot water - BaA'. xaq -AgC₁₈H₁₃O₅ curdy pp

C.H. CH C-CH CH. >C.H. [256°] Optained by heating the lactonic acid at $13\tilde{0}^{\circ}$ Crystals, insol water, Na₂CO₂Aq, and Yields an unstable dibromide NaOHAq

a 0XY-β-PHENYL-180-BUTYRIC ACID CH,Ph CMe(OH) CO2H [99°] Made by the action of KCy on the bisulphite compound of benzyl methyl ketone, the product being saponi fied (Gabriel a Michael, B 12, 814) Long prisms, sol water and alcohol

β-Oxy-β-phenyl-isobutyric acid CHPh(OH) CHMe CO.H [125°] Formed by reducing a benzoyl-propionic acid with sodiumamalgam (Perkin, jun, a Calman, C J 49, 161) Needles, v e sol hot water -AgA' crystals

β-0xy-γ-phenyl-butyric acid CH₂Ph CH(OH) CH₂ CO₂H [98°] Formed by boiling phenyl-isocrotonic acid with NaOHAq (Fittig, B 24, 84) Flat needles.

y-Oxy-y-phenyl-butyric acid CHPh(OH) CH, CH, CO,H 'Benzhydrylpro-pronuc acid' [75°] Formed by reducing benzoylpropionic acid with sodium-amalgam (Burcker, Bl [2] 87, 5, A Ch [5] 26, 455), and also by boiling its lactone with baryta Flat crystals (from CS₂), splitting up at 70° into water and lactone Chromic acid mixture oxidises it to benzoyl propionic acid —BaA'₂ —CuA'₂ —AgA' crystalline pp

Lactors CHPh (0-CO) [37°] (306°) Formed from γ bromo γ -phenyl butyric acid by treatment with Na₂CO₂ or boiling with water (Jayne, A 216, 103) Formed also by boiling phenyl paraconic acid with diluted (1 1) H_2SO_s (Erdmann, A 228, 178) Six sided trimetric tables (from CS_2), abc=611 1 426 It has a pleasant odour, and is volatile with steam

Amade CHPh(OH) CH2 CH2 CO NH2 [86°] Formed by heating the lactone with alcoholic NH_s at 100° (Fittig, A 256, 155) Monoclinic prisms, v sol hot water Forms unstable

C10H13NO2HCl, crystallising in needles

o Oxy phenyl butyric acid Methyl derivative C₆H₄(OMe) C₃H₆ CO₂H [56°] tained by reducing either (a)- or (b) methoxyphenyl crotonic acid with sodium amalgam (Perkin, C J 39, 433) Transparent prisms (from light petroleum) May be distilled— BaA', (dried at 100°)

α-Oxy-di phenyl-isobutyric acid v Di

BENZYL-GLYCOLLIC ACID

γ-0xy-di-γ phenyl butyric acid

CPh₂(OH) C₂H₄ CO₄H [145°] Made from its lactone (Auger, A Ch [6] 22, 316) Thin leaflets (from alcohol) Changes to lactone on melting, but is stable at 100°—BaA'₂ micaceous plates, sol water

Lactone CPh2 CH2CH2 [90°] Formed by the action of succinyl chloride on benzene in presence of AlCl. Leaflets, insol water, sl sol cold alcohol

Oxy-tri-phenyl-butyric acid

CHPh(OH) CH₂ CPh₂ CO₂H Formed by reducing di-phenyl-benzoyl propionic acid in alkaline solution with sodium amalgam (Japp a Klingemann, C J 57, 680, B 22, 2882) White solid, sol Na₂CO₃Aq

Lactone $C_{22}H_{18}O_2$ [153°] Small needles,

sol hot alcohol.

βγ Di-oxy-γ-phenyl butyric acid CHPh(OH) CH(OH) CH₂ CO₂H [118°] Made from its lactone, which is got by oxidising phenyl isocrotonic acid with KMnO₄ (Fitting, B 21, 920) Crystals, forming the lactone on melting

Lactone CHRh COCO CH(OH) CH2 [87°]

Melts when hydrated (with \(\frac{1}{2} \) aq) at 77°

Di oxy phenyl butyric acid

Methyl derivative [4 1] C.H. (OMe) CH(OH) CH2 CH2 CO2H Got from its lactone [53 5°], which is made by the action of sodium amalgam on brome p methoxyphenyl-butyrolactone (Fittig a Politis, A 255, 299) The free acid is solid, and yields the lactone when heated to 80° —BaA', amorphous

Di-oxy-phenyl-isobutyric acid

Methyl derivative C_cH_s(OH)(OMe) CH_cCHMe CO_cH Hydrohomo-ferulic acid [115°] Obtained by reducing C_cH_s(OH)(OMe) CH CMe CO_cH (Tiemann a.

Kraaz, B 15, 2070) Sol water, alcohol, and ether

Di-methyl derivative C_aH₃(OMo), CH, CHMe CO,II Methyl hydrohomoferulic acid [59°] Got in like manner

Methylene derivative C₈H₃(O₂CH₂) CH CHMe CO H Hydrohomo-caffec acid [77°] Formed by reduction of the methylene derivative of dioxy phenyl methacrylic acid (Lorenz, B 13, 760) Thick prisms, sl sol water, v sol alcohol and ether Di-oxy di phenyl butyric acid?

CH, CPh(OH) CPh(OH) CO H I ormed from its nitrile, which is made from acetophenone, KOH. and aqueous KaFeCy, (Buchka, B 20, 389) -

BaA', 3 laq

o-OXY-PHENYL-CARBAMIC ACID Ethyl ether C,H₁₁NO, i.e C,H₁(OH) NH CO₂Et [85°] Formed from o amido phenol and ClCO₂Et (Groenvik, Bl [2] 25, 177) Triclinic prisms (from ether alcohol), almost insol cold Yields, on distillation, alcohol and the anhydride

C.H. COSC OH Oxycarbanil Oxymethenyl

amidophenol Anhydro o amido phenyl carbonic Carbonyl amido phenol [1386] (above acud360°)

Formation -1 As above -2 By heating oxy phenyl urea (Kalckhoff, B 16, 1828) -3By distilling o amido phenyl ethyl carbonate (Bender, B 19, 2269, 2950)—4 By heating a mixture of urea and o amido phenol (Sandmeyer, B 19, 2655) -5 By the action of phosgene on o-amido phenol in benzene (Chetmicki, B 20, 177, Jacoby, J pr [2] 37, 29) —6 By heating o amido phenyl di phenyl carbamate (Lellmann a Bonhoffer, B 20, 2126)

Properties - Needles (from water), sol al cohol, ether, and alkalis Decomposed by heating with HClAq above 150° into CO and o amido phenol Bleaching powder and HCl

yield crystalline $C_sH_3Cl < NCl > CO$, whence

further action of HClAq forms $C_0H_3Cl < {}^{\rm NH}_O > CO$ [196°] Br forms C,H,BrO,(NH) [196°] HNO,

produces C₇H₂(NO₂)O₂NH [256°] Injected into rabbits, it becomes $C_sH_s(OSO_sH) < {}^{NH}_O > CO$

(Nencki, M 11, 253) —AgC,H4NO2 curdy pp Acetyl derivative C,H4O2NAc [98°] Crystallises from water

Phenyl-hydraside

 $C_0H_4 < N_2HPh$ [208°] Yellow needles

Ethyl derivative C.H. NEt >00.

(300°) Formed from the silver salt and EtI Crystalline Converted into ethyl amidophenol by heating with fuming HClAq at 180°

Ethyl ether C.H. 230°) Formed from amido phenol hydrochloride and NH C(OEt)2 (Sandmeyer) Liquid, converted by HClAq into EtCl and C.H. NH>CO

p-Oxy phenyl-carbamic acid Ethyl ether $C_0H_{11}NO_3$ is $C_0H_4(OH)$ NHCO₂Et [120°] Formed from p amido phenol and ClCO₂Et (Groenvik, Bl [2] 25, 179) Monoclinic tables, v sol alkalis The ethyl derivative C.H.(CEt) NHCO2Et, formed from ClCO2Et and $C_0H_4(NH_2)(OEt)$ (Köhler, J pr [2] 29, 257), ciystallises in needles [94°], insol water

Reference - Chloro oxy-Phenyl carbamic

p **OXY-DI-PHENYL-CARBINOL** $C_{13}H_{12}O_2$ to C_8H_5 CH(OH) $C_8H_4(OH)$ [161°] Formed by Formed by reducing oxy benzophenone with sodium amal gam (Doebner A 210, 253) Silky needles (from water) Coloured red by FeCl,

op-Dı oxy di-phenyl carbınol

CH(OH)(C₆H, OH)₂ [160°-165°] Made by reducing di oxy benzophenone (salicyl phenol) Made by with sodium amalgam (Michael, B 14, 657)
Amorphous powder, sol hot alcohol

Di oxy tri phenyl carbinol

C_sH_sC(OH)(C,H,OH)₂. [c 100°]. Made by warming PhCCl, with dry phenol, and treating the product with water (Doebner, A 217, 227) Formed also by warming phenyl glyoxylic acid with phenol and H₂SO, at 120° (Homolka, B 18, 988) Brick red powder, insol cold water, melts under hot water Its alcoholic solution dyes silk feebly yellow In alkalis it dissolves with deep violet red colour, and is reppd by acids

Di acetyl derivative $C_6H_5C(OH)(C_6H_4OAc)_2$ [119°] Colourless prisms (from dilute alcohol)

Tri oxy tri phenyl carbinol Anhydride C₁₉H₁₄O₃ re (C₃H₄(OH))₂C<C₀H₄> Aurin

Rosolic acid

Formation - 1 By heating phenol with ovalic acid and H2SO, (Kolbe a Schmitt, A 119, 169, Dale a Schorlemmer, A 196, 79) -2 By heating phenol with formic acid and ZnCl, at 120° (Nencki a Schmid, J pr [2] 23, 549, 25, 273) —3 By the action of AlCl₂ on a mixture of phenol and tri chloro nitro methane (Elbs, B 16, 1275) -4 From para rosaniline by the diazo reaction (Fischer, A 194, 268) -5 From di p oxy benzophenone by treatment with PCl,, and heating the product with phenol and H SO,

(Caro a Graebe, B 11, 1350)

Preparation — Phenol (10 pts) is heated with dried oxalic acid (7 pts) and H,SO, (5 pts) at 120°-130° about 24 hours, until gas no longer comes off rapidly The product is poured into water, the pp dissolved in NaOHAq, saturated with SO,, and mixed with much water The filtrate from ψ rosolic acid (which amounts to 70 p c of crude product) is saturated at 70° with HCl, and on cooling it deposits aurin sulphite This is recrystallised from dilute alcohol, which deposits methyl aurin on cooling, while the mother liquor, saturated with SO2, deposits aurin sulphite, which is freed from SO, by heat (Zulkowsky, A 194, 119, 202, 184)

Properties - Dark red trimetric crystals (from alcohol HOAc) or red needles with green lustre (from alcohol) Not melted below 220° Its alkaline solution is crimson

Reactions -1 Reduced by sinc-dust and HOAc to tri-oxy-tri phenyl methane—2 Aqueous NH, at 120° yields para-rosaniline.—3.
Vol. III

Water at 250° yields phenol and di p-oxy benzophenone—4 On warming with KOHAq and KCy and adding HCl, a product is got which, when heated with Ac.O, yields tri-acetyl hydrocyanaurın [194°]

Salts—(NH₄)₂C₁₈H₁₂O₃ dark red needles with steely lustre—C₁₀H₁₀O₄HCl1¹₂HOEt red crystals—(C₁₀H₁₄O₄HCl)HOAc red needles—(C₁₀H₁₄O₃)₂H₂SO₃4aq brick red cubes, sl sol cold alcohol—C₁₀H₁₄O₃(NH₄)HSO₃— Cl₁₈H₁₄O₃NaHSO₃ — Cl₁₈H₁₄O₃KHSO₃ colourless tables — Cl₁₈H₁₄O₃KHSO₄ — (Cl₁₈H₁₄O₃)₂H₂SO₄ blush violet needles.

Dracetyl-derivative minute

(C,H,(OH))2C(OAc) C,H,OAc [168°] Formed from aurin and Ac₂O at 100° Colourless tables (from alcohol)

Tetra-oxy-tri-phenyl-carbinol

C19H18O, 16 C9H3C(OH)(C6H3(OH)2)2 Anhydride C₃₈H₃₀O₉ Resorcin benzein. Formed by heating benzo trichloride with resorcin at 180° (Doebner, B 13, 610, A 217, 234) Large crystals (from alcohol and HOAc) Yellow by transmitted, violet red by reflected light, at 130° it loses 2H,O, and at 200° it is decomposed Dilute alkaline solutions show yellowish green fluorescence, but less intense than fluorescein, they dye wool yellow Insol water, v sol alcohol Zinc dust and HCl reduce it to tetra oxy tri phenyl methane Bromme in alcohol and HOAc forms a fiery red pp C₃₈H₂Br₈O₉, which closely resembles eosin salts dissolve readily in alcohol and dye wool and silk like eosin

Penta-oxy-tri-phenyl-carbinol

(C₆H₃(OH)₂)₂C(OH) C₆H₄OH Anhydride C₁₉H₁₄O₆ Anhydride C₁₉H₁₄O₅ Formed by heating resolution with formic acid and ZnCl₂ at 140° (Nencki a Schmid, J pr [2] 23, 547)

scopic brick red powder, v sol alcohol p OXY-DI-PHENYL-CARBINOL o-CARB-OXYLIC ACID

Methyl derivative of the anhydride CH C,H, OMe Coo [1170] Formed by re-

ducing methoxy benzophenone carboxylic acid with zinc and alcoholic HCl (Nourrisson, B 19, 2103) Flat white needles, v sol warm alcohol, msol water

Oxy-tri-phenyl-carbinol carboxylic acid Anhydride C,H,(OH)CPh

Oxy di phenyl phthalide [155°] Prepared by heating o benzoyl benzoic acid with phenol and SnCl, to 120°, yield 100 pc of the benzoylbenzoic acid (Pechmann, B 13, 1613) Colourless crystals Sol all ordinary solvents except water and ligroin By fusion with KOH it gives benzoic acid and oxy-benzophenone With alkalis it forms a deep-red solution By strong H₂SO₄ it is converted into oxy-phenyl anthranol O_eH_4 $C(O_eH_4OH)$ O_eH_4 On reduction it gives oxy triphenyl methane carboxylic acid

Acetyl derivative C20H12O2(OAc). [186°]. Colourless crystals

Di-bromo- derivative C20H11Br2O2(OH).

[196°] Spikes Acetyl de bromo-derivative

C₂₀H₁₁Br₂O₂(OAc) [172°] Colourless prisms.

ap - di - oxy - di - phenyl - carbinol carboxylic | anhydride Methyl derivative

 $C_{o}H_{o} < CH(C_{o}H_{o}OMe) > .$ [117°] Made by re ducing 'p anisolphthaloylic' acid (Nourrisson, Bl [2] 46, 206) Needles, msol water, v e sol

Di-oxy-tri-phenyl-carbinol carboxylic acid Anhydride C,H,(OH)2CPh COH,

Benzene resorcin phthalein [176°] Made by heating benzoyl benzoic acid with resorcin (Pechmann, B 14, 1859) Prisms (containing CHCl₂) melting at 114° (from chloroform) Its alcoholic solution turns greenish blue on addi tion of HCl On heating with H2SO4 it yields anthraquinone. H2SO4 acting on its solution in HOAc forms $C_{40}\dot{H}_{20}O_7$ [285°], which yields $C_{40}\dot{H}_{24}\Delta c_2O_7$ [245°]

Di acetyl derivative C20H12O2(OAc)2. [137°]

Di-bromo- derivative C20H12Br2O4 [219°]

Tri-oxy-tri-phenyl-carbinol-carboxylic acid Anhydride (C₆H₂(OH)₃)CPh CO

Bensene pyrogallol-phthalein Prepared by heat ing benzoyl benzoic acid with pyrogallol and crystallising the product from acetic acid (Pech mann, B 14, 1864) Four-sided tables (containing AcOH), [190°] Sol most solvents except ligroin, sl sol hot water It dissolves in alkalis with a green colour

Tri acetyl derivative C₂₈H₁₁O₂(OAc)₂.
[231°] Fine needles Sol Ac₂O

DI-OXY DI-PHENYL-CARBOLACTONE ISO-EUXANTHIC ACID

OXY-DI-PHENYL-DI-CARBOXYLIC Hexahydride O14H16O5 An unstable acid formed by boiling hydro oxybenzyluric acid with potash (Otto, A 134, 330) Yields Et2A" (206°), a heavy oil

D1-p-oxy-diphenyl carboxylic acid C15H10O4 s.e. [4 1] $C_0H_4(OH)$ $C_0H_3(OH)(OO_2H)$ [1 4 2] [270°] Made by fusing diphenylene ketone disulphonic acid with potash (Schmidt a Schultz, B 12, 496) Sl sol water, v sol hot alcohol

Di p-oxy-diphenyl dicarboxylic acid $C_{4}H_{3}(OH)(CO_{2}H)C_{4}H_{3}(OH)CO_{2}H$ [151°] 0052 at 15°. Formed by heating sodium di oxy di phenyl with CO₂ at 200° under high pressure (Schmitt a Kretzschmer, B 20, 2703) Minute needles, sl sol water. FeCl, colours its solution bluish violet

Tetra oxy-diphenyl dicarboxylic acid C₄H₂(OH)₂(CO₂H) C₄H₂(OH)₂CO₂H Di resorcin dicarboxylic acid Formed by heating tetra-oxy diphenyl (diresorcin) with KHCO₂ and a little water at 130° (Will a Albrecht, B 17, 2105) Yellowish powder, decomposing, without melting, above 800°.—K₂A".—BaA" 6aq —Ag₂A". white pp

Tetra-oxy-diphenyl dicarboxylic acid C₀H₂(OH)₂(CO₂H) C₀H₂(OH)₂(CO₂H) diprotocatechnic acid [above 300°] Dehydro-Formed by fusing 'dehydrodivanillin' with potash (Tiemann, B 18, 3495). Amorphous, v. sl. sol water, sl sol alcohol

Penta-oxy-diphenyl carboxylic acid C₁₄H₁₆O₅ Formed by the action of POCl₅ on e-tri oxy-benzoic acid (Schiff, G. 17, 552, A.

245, 87) Yellowish astringent powder —BaA'.: greyish white powder

Penta-acetyl derivative C,4H,Ac,O, White powder, rapidly darkening in air

Ethyl ether EtA' [102]

Penta-oxy dı phenyl carboxylic acid 4. C14H10O2 Formed by heating phloroglucin carb-

oxylic acid with POCl, (Schiff) Reddish brown hygroscopic mass, resembling tannin and the preceding isomeride

TETRA-OXY-DIPHENYL DICARBOXYLIC

ALDEHYDE D:-methyl derivative C_sH₂(OMe)(OH)(CHO) C_sH₂(OMe)(OH) CHO Divanilin [304°] Formed by boiling vanillin CaHa(OMe)(OH)(CHO)[3 4 1] with FeCl, (Tie mann, B 18, 3493) Slender white needles, sl sol alcohol, sol alkalıs

Tetra methyl derivative [138 p OXY-PHENYL-CINNAMIC ACID

Me. thyl derivative C₆H₄(OMe) CH CPh CO₂H Formed from sodium phenyl acetate, anisic aldehyde, and Ac₂O (Oglialoro, G 9, 533, 10, 481) Prisms (from alcohol), sl sol water
α ΟΧΥ-γ PHENYL-180 CROTONIC ACID

C₆H₅ CH CH CH(OH) CO₂H [115°] by boiling cinnamic aldehyde with aqueous HCy and HCl (Matsmoto, B 8, 1144, Peine, B 17, 2114) Formed also by heating the ethyl ether of styryl \(\psi\) hydanto in with concentrated baryta water (Pinner a Spilker, B 22, 690) Styryl \u2214

hydantom CHPh CH CHCONH [198°] 18 obtained by the action of warm alcoholic potash on styryl hydantoïn [172°], an isomeric body previously described by Pinner $(B\ 20,\ 2353)$ as oxystyryl pyrazole Styryl hydantom is got by the action of boiling dilute HClAq on (a) ur amido phenyl crotonic nitrile

CHPh CH CH(NH CO NH₂) CN [160°], which is made by heating oxy phenyl isocrotonic nitrile with urea

Properties - Needles, sl sol cold water, v sol alcohol and ether

Salts -PbA', 2aq needles -AgA' minute needles

Methyl ether MeA'. (290°) Lig Ethul ether EtA' (295°) (Peine)

CHPh CH CH(OH) CN [81°1 Nitrile Formed from cinnamic aldehyde, KCy, and HCl Crystalline grains (from benzene ligroin) Con verted by hydroxylamine into the crystalline CHPh CH CH(OH) C(NH₂) NOH amidoxim (Bornemann, B 19, 1513)

o-Oxy-phenyl-crotonic acıd (a) Methyl derivative C.H. (OMe)CH CMe CO.H [1180] Made from its methyl ether by boiling with alcoholic potash (Perkin, C J 33, 213, 39, 431) Monoclinic crystals (from alcohol), = 863 1 1 252, β = 64° 54′ (Fletcher) Not converted into its (β) isomeride by light With PCl, it gives MeCl, HCl, and the anhydride Conc H₂SO₄ also forms propionic coumarin Sodium amalgam reduces it to methoxy phenyl butyric acid. With Br and with HI it behaves like the (β) acid

Methyl ether of the (a)-methyl derivative CoH (OMe) CH CMe COH (275°) SG 15 1 1112, 36 1 1061 Formed from sodium propionic coumarin and Mel Liquid

(β) - Methyl derivative O_cH₄(OMe)CH.OMe CO₂H Formed from methyl salicylic aldehyde, sodic propionate

and propionic acid

Properties - Monoclinic crystals, a b c = 1 281 1 762 β = 84° 18' (Fletcher) With PCl, it gives the chloride of the acid Cone H.SO, appears to polymerise it Behaves like the (a) isomeride with sodium amalgam. With dry bromine vapour it forms the compound C_eH_eBr₂(OMe)CHBr CMeBr CO₂H [c 200°] With HI (S G 1 94) it unites, forming a product whence Na₂CO, liberates the methyl derivative of callyl phenol—AgA' white pp

Methyl ether of the (β)-methyl derivative MeA' (c 286°) SG 18 11279, 36

1 1136

(β) Ethylderivative

C, H, (OEt)CH CMe CO2H [193°] Formed from ethyl-salicylic aldehyde, sodic propionate, and propionic anhydride Large tables (from alcohol) Its Ba salt forms satiny needles

Anhydride C.H. CH CMe Propionic coumarın Methyl-coumarın [90°] (292 5°) Formed by heating sodium salicylic aldehyde with propionic anhydride (Perkin, C = J = 28, 10) Trimetric crystals, $a \ b \ c = 2 \ 1950 \ 1 \ 4001$ Smells like coumarin, m sol alcohol, nearly insol cold KOHAq Fuming H₂SO₄ forms C₁₀H₂O₂(SO₂H) whence BaA', 10aq

Oxy-phenyl-crotonic acid Anhydride C.H. CMe CH B Methyl coumarin Formed by the action of H2SO, on a mixture of acetoacetic ether and phenol (Pechmann a. Duisberg, B 16, 2127)

p-Oxy-phenyl-crotonic acid Methyl derivative C₆H₄(OMe) CH CMe CO₂H [154°] Formed from anisic aldehyde, sodium pro pionate, and propionic anhydride Rectangular

tables (from alcohol) -- AgA

p Oxy-phenyl-isocrotonic acid Methyl derivative C.H. (OMe) CH CH CH, CO.H [1065°] Formed by heating anisic aldehyde with sodium succinate and Ac,O at 120° (Fittig a Politis, A 255, 294) Plates, m sol hot water -BaA', 3aq -CaA', 2aq -AgA sol hot

γ-Oxy-tri phenyl crotonic acid Lactone C₂₂H₁₆O₃ re CH CPh CO (?) [118°] 329 (by Raoult's method), 312 (calc) Formed by heating αβ di benzoyl styrene at 310° (Japp a Klingemann, C J 57, 679, 702, 59, 148) Lustrous needles or monoclinic prisms attacked by phenyl hydrazine or Ac.O at 150° Bromine forms C₂₂H₁₃BrO₂ [109°] Chromic acid mixture oxidises it to benzophenone May be reduced to oxy tri phenyl butyric acid Alcoholic potash at 100° yields CH, Bz CPh, CO, H, which at 310° changes to the original lactone Alcoholic methylamine forms CH₂Bz CPh₂CONHMe [156°] Ethylamine acts in like manner

y Oxy-tetra phenyl-crotonic acid. Lactone CPh CPh CO Tabular oxylepiden [186°] S CPh CO Tabular oxylepiden [186°] S (alcohol) 7 at 78° Formed by heating 'accoular oxylepiden ' CPhBz CPhBz at 340° (Zinin, J R 5, 16, Bn. 8, 118, Japp a Klingemann, C. J. 57, 665, Klingemann a Laycock, C J. 59, 140) Tables (from alcohol) . msol. water. Converted by alcoholic potash into C_nH_nKO_s. Methyl-

amine in alcohol at 100° forms CHPhBz CPh. CONHMe [267°] crystallising in triclinic plates

D1 oxy-phenyl-crotonic acid C_eH₂(OH)₂ CMe CH CO₂H. (β) methyl-umbellec acud

Methyl derivative [4 2 1] C_eH₂(OH)(OMe) CMe CH CO₂H [140°] Formed by boiling the methyl derivative of (β)methyl umbelliferon with conc KOHAq for 5 hours (Pechmann a. Duisberg, B 16, 2125). Four sided tables, insol water, v sol. alcohol. Reconverted into its lactone by boiling with acids or heating with NH,Aq

Di-methyl derivative C₆H₃(OMe)₂ CMe CH CO₂H [145°] Formed by saponification of its methyl ether (310°-320°) which is obtained by further methylation of the methyl derivative (Pechmann a Cohen, B 17. 2132) Small needles, v sol alcohol -AgA'. white powder

Anhydride C₆H₃(OH) < OMe CH CO

Methyl umbelliferone [186°] Formed by the action of H2SO, on a mixture of acetoacetic ether and resorcin (Pechmann a Duisberg, B 16, 2119, A 261, 169, of Schmid, J pr [2] 25, 82) Formed also by warming acetoacetic ether with resorcin and alcoholic potash, and heating the resulting methyl-umbelliferone carboxylic acid [191°] above its melting point (Michael, J pr [2] 37, 469) (3) methyl umbelliferone is also obtained by heating citric acid with resorcin and H₂SO₄ (Wittenberg, J pr [2] 24, 125) Plates (by sublimation), sol alcohol and hot water, sl sol ether Its dilute alkaline solution has blue fluorescence Potashfusion forms di oxy acetophenone Yields a nitro compound, converted by reduction into amido-(\$\beta\$) methyl umbelliferone [247°], whence B',H,SO, 2aq and $C_{10}H_8(NO)NO_3$ Sodium-amalgam reduces (β)-methyl umbelliferone to $C_{10}H_{10}O_3$ [259°], whence C₁₀H₉AcO₃ [222°] (Michael, Am. 5, 436)

Acetyl derivative of the anhydride C12H10O4 [150°] Long white needles, v sol. alcohol

Benzoyl derivative of the anhydride C_{1e}H BzO, [160°] Needles (from alcohol)

Methyl derivative

 $C_6H_3(OMe)$ $< CMe CH \\ O - CO$ [159°] Needles (from alcohol), msol water On reduction with sodium amalgam it yields $C_0H_1(OMe) < CHMe CH_2 CO CO$ [244°] Bromine in chloroform reacts forming $C_sH_s(OMe)$ < CMeBr CHBr [235°]

(4 3 1) Di-oxy-phenyl-crotonic acid Home- $C_eH_a(OH)_2$ CH $C(CH_3)$ CO₂H [4 3.1] caffere acid

p-Propionyl-m methyl derivative C.H. (OCO C.H.) (OMe) CH C(CH.) CO.H Propiohomoferulic acid [129°] Formed by heating vanillin with sodium propionate and prepionic anhydride (Tieman a. Kraaz, $B\,$ 15, 2060). White needles, sol alcohol, ether, and benzene, insol water and ligroin.

m-Methyl derivative C.H.(OH)(OMe).CH C(CH.) CO.H. Homoferules

acid [168°]. Large trimetric tables Sol alcohol and ether, sl. sol chloroform, benzene, and hot water, nearly insol cold water and ligroin. On heating the acid it splits off CO₂ forming iso-eugenol —A'₂Ba yellow needles. Dr methyl derivative

C_eH_s(OMe), CH C(CH_s) CO₂H Methyl-homoferulic acid [141°] Needles Sol alcohol, ether, and hot water -A'Ag white crystalline pp

Di-methyl-derivative-methyl ether C₆H₃(OMe)₂.CH C(CH₃) CO₂Me [66°] Colourless plates

Methylene derivative

CH₃<0>C₆H₃ CH CMe CO₂H [194°] Formed

by boiling piperonal with propionic anhydride and sodium propionate (Lorenz, B 13, 759) Prisms (from dilute alcohol) -AgA'

Tri-oxy-phenyl-crotonic acid Anhydride $O_0H_2(OH)_2$ CMe CH CO - CO[235°] Prepared by the action of H2SO, on a mixture of acetoacetic ether and pyrogallol (Wittenberg, J pr [2] 26, 68, Pechmann a Duisberg, B 16, 2127) Needles, sol. alcohol and hot water. Coloured green by FeCl. Yields a di-acetyl derivative [176°] isomeride [284°] is formed by using phloroglucin instead of pyrogallol, it yields a di acetyl derivative [140°] (Pechmann a Cohen, B 17, 2189)

Tetra-oxy-phenyl-crotonic acid. Methulens-dr-methyl derivative

CH₂<0>C₆H(OMe)₂.CH CMe CO₂H. [2099]. Formed by heating apionic aldehyde with propionic aldehyde and sodium propionate (Ciamician a Silber, B 22, 2488) Yellow needles, almost insol water -CaA', 5aq -AgA' white gelatinous pp

OXY-PHENYL-CUMINYLAMINE v CUMINYL-AMIDO-PHENOL

OXY-PHENYL CUMYLAMINE v CUMINYL ÍDENE-AMIDO-PHENOL

o-OXY-PHENYL-CYANAMIDE Ethyl de-[94°] Made by rivative C.H.(OEt)NH Cy passing gaseous ClCy into an ethereal solution of o-amido phenetole (Berlinerblau, J pr [2] 30, 100). Crystals Insol water, v sol alcohol and ether. Does not appear to polymerise Wifuming HOl at 120° it gives o amido phenol

Salts -C,H,N,ONa Microscopic needles, got by mixing alcoholic solutions of NaOEt and ethoxy phenyl cyanamide Its aqueous solution does not absorb CO₂ —C₂H₂N₂OAg Curdy pp

p-0xy-phenyl-cyanamic tive C_eH₄(OEt)NHCy. [78°] Made in the Colourless crys-Insol water, v sol. alcohol and ether-C.H.N.OAg.

OXY-PHENYL-CYANATE, Ethylderivateve C.H. (OEt) N CO [219°] Made by distilling C.H. (OEt) NH CO.Et (Köhler, J. pr. [2] 29, 259) White needles (from HOAc), sol alcohol and chloroform

DI-OXY-PHENYL-DI-CYMYL-METHANE OHPh(O,H,MePrOH). [146°] Formed from benzoic aldehyde, thymol, and H.SO. (Russanoff, B 22, 1949). Thin tables (containing EtOH), v. sol. chloroform

Di-acetyl derevative [126°]. Crystals

OXY-DIPHENYLENE-ACETIC ACID

 $<_{O_aH_a}^{O_aH_a}>O(OH) CO_aH.$ [162°] Formed by boiling phenanthraquinone with NaOHAq (Baeyer, B 10, 125, Friedlander, B. 10, 584) NaOHAq Plates (containing $\frac{1}{2}$ aq), v sl sol cold water, v sol alcohol Cone H_2 SO, forms a blue solution on warming Chromic acid mixture yields di-phenylene ketone NaOHAq at 160° splits it up into fluorene alcohol and CO₂. HIAq and P on warming at 140° reduce it to diphenylene acetic acid Bromme forms O₁H₂Br₂O₂ [225], whence O₁₄H₂Br₂EtO₃ [151°] — CaA'₂2aq crystals Ethyl other EtA' [92°] 'Prisms. DI-OXY-PHENYLENE-DIAMINE

C₆H₂(OH)₂(NH₂)₂ Got by reducing the dioxim of di oxy-quinone with SnCl, and HCl (Nietzki a Schmidt, B 22, 1656) Yields on oxidation orystalline C₆H₂(OH)₂(NH)₂ —B'H₂SO₄

Tetra-acetyl derivative [225°] Needles. Isomeride v Di-AMIDO HYDROQUINONE

DI-OXY-DIPHENYLENE-DIHYDRAZINE $C_6H_3(OH)(N_2H_3)C_6H_3(OH)(N_2H_3)$ $[140^{\circ}]$ Formed by reducing the diazo- compound from di-oxy di amido-diphenyl with SnCl₂ (Kunze, B 21, 3333) Thin plates, forming with acetone a compound $O_{18}H_{22}N_1O_2$ [200°] OXY-DIPHENYLENE KETONE $O_{19}H_4O_2$ is

 $CO < \stackrel{C_0H_4}{C_6H_5}OH^{\bullet}$ [96°] (G), [91°] (R) Formed by warming dry sodium salicylate with excess of POCL, and distilling (R Richter, J pr [2] 28, It is also one of the products of the action of phenol on the sulphate of o diazo benzoic acid (Griess, B 21, 981) Needles, insol water, v sol hot alcohol Its vapour passed over red-hot lime yields diphenylene ketone and dı phenylene ketone oxıde [82] Dıstılled over red hot zinc dust it is reduced to diphenyl Gives a nitro-derivative [224°], a di nitro deri vative [c 235°], and a bromo derivative [193°]

OXY - DIPHENYLENE - KETONE OXIDE $C_{12}H_6O_3 \text{ is } C_6H_4 < {\stackrel{\textstyle O}{\bigcirc}} > C_6H_4(OH) \quad \textit{Oxy-xanth-}$ [147°] Formed by heating resoroin with salicylic acid and ZnCl2 (Michael, Am 5, 91). Formed also by heating salicylic acid with (β) resorcylic acid and Ac₂O (Graebe, A 254, 290) Yellow needles (from alcohol) Split up by fusion with potash into resoroin and salicylic acid. Gives diphenylene methane oxide [99°] when distilled with zinc dust Yields tri oxy-benzophenone [183°] when fused with NaOH - $NaC_{13}H_{2}O_{3}$ — $Na_{2}C_{13}H_{8}O_{4}$ (dried at 100°) Lemonyellow needles

Acetyl derivative C₁₃H,AcO₂ [168°]. Di-oxy-diphenylene ketone oxide v EUXAN-THONE, vol 11 p 529 (β)-Iso euxanthone C₆H₈(OH) < O > C₆H₈(OH), got from di nitrodiphenylene ketone oxide [260°], yields a crystalline di-acetyl derivative [175°] (Graebe, A. 254, 801) An isomeride O₆H₄<0>C₆H₂(OH)₈ [247°] is obtained from phloroglucin and salicylic acid (von Kostanecki a Nessler, B 24, 1896). A second isomeride with the formula $C_{c}H_{c}<_{CO}^{O}>C_{c}H_{c}(OH)_{2}\begin{bmatrix}1&6\\2&6\end{bmatrix}$ [240°], got by heating tetra-oxy-benzophenone with water at 2000 yields a diacetyl derivative [161°] and dyes cotton mordanted with alumina, yellow, and with iron, greyish black (Graebe, B 24, 969) Another isomeride $\begin{bmatrix} 1 & 3 \\ 4 \end{bmatrix}$ $C_0H_3(OH) < \begin{matrix} O \\ CO \end{matrix} > C_0H_3(OH) \begin{bmatrix} 1 \\ 25 \end{bmatrix}$ [246° cor] made by heating resorcylic acid with Ac vields a diacetyl derivative [c 127°] (G).

Tetra oxy-diphenylene ketone oxide v An-

hydride of Hexa OXY-BENZOPHENONE DI-OXY PHENYLENE-DI METHYL DIKE-TONE C_eH₂(OH)₂(CO CH₂)₂. [180°] Obtained from di oxy acetophenone (10 g), ZnCl₂ (20 g), HOAc (50 g), and POCl, (10 g), at 140° (Cre pieux, Bl [3] 6, 152) Crystals (from hot water), yields with phenyl hydrazine the compound C.H. (OH), (OMe N.HPh), [c 231°]

Tri oxy-phenylene di-methyl diketone

C₆H(OH)₂(CO CH₂)₂ [189°] Formed in like manner from tri oxy acetophenone (C) Yields a di phenyl di hydrazide [246°] and also an acetyl derivative [209°] which yields a di phenyl

dı hydrazıde [265°

DI OXY PHENÝLENE DI PHENYL DIKE TONE $C_{20}H_{14}O_4$ is $C_6H_2(OH)_2(CO C_6H_5)_2$ Dibenzoresorcin [149°] Formed, together with dioxybenzophenone, by heating resorcin with BzCl and ZnCl₂ (Doebner a Stachmann, B 11, 2270, A 210, 259) Leaflets, insol water

Di acetyl derivative [150°] Needles Di benzoyl derivative [151°] Needles Di oxy phenylene di phenyl diketone

C₆H₂(OH)₂(CO C₆H₃)₂ Dibenzohydroquinone [207] Formed from hydroquinone, BzCl, and AlCl. (D) Golden needles (from alcohol)

Di-bensoyl dermative [146°] Plates TETRA OXY DIPHENYLENE DI PHENYL-DI THIO-DI UREA Tetra methyl deriva-

 $\label{eq:complex} {\rm NHPh.CS~NH~C_0H_2(OMe)_p.C_0H_2(OMe)_p.NH~CS~NHPh.}$ Formed by warming the compound C₆H₂(OMe)₄(NH) C₆H₂(OMe)₂(NH₂) with phenylthiocarbimide (Bossler, B 17, 2128) Flakes, sol

TETRA - OXY - DIPHENYLENEQUINONE

Tetra methyl cther v Cerulignon
DI OXY DIPHENYLENE QUINOXALINE Ds ethyl ether

 $\left[6\ 3\ {}^{2}_{1} \right] C_{e} H_{2} (OEt)_{2} < \stackrel{N}{N} \stackrel{C}{C} \stackrel{C}{C}_{e} H_{4} \stackrel{[1\ 2]}{[1\ 2]}$ [260°] Formed by the action of phenanthraquinone on the hydrochloride of the diethyl ether of (a)diamido hydroquinone (Nietzki a Rechberg, B 28, 1212) Yellowish needles, al sol water

OXY DI-PHENYL ETHANE

O, H,O C.H. CH.CH.C.H.(OH) r.e Formed by CH, CH(C,H,) C,H,(OH) [58°] allowing a mixture of styrene, phenol, H2SO4, and HOAc to stand (Koenigs, B 28, 8144) Crystals, sol dilute NaOHAq

Bensoyl derivative [83°]

Methyl derivative CH2Ph CH2C.H4OMe [61°] Formed from a-phenyl methoxy cinnamic acid, alcohol, and Na (Freund a Remse, B. 28, 2865) Plates, sol alcohol

Sulphonic acidC1.H12(OH)(8O.H Formed by potash-fusion from s-di phenylethane disulphonic acid (Kade, B 7, 289) Plates, sol hot water

Di-p oxy-s-di phenyl-ethane O,H,(OH) OH, OH, C,H,(OH) [189°] from di-phenyl-ethane disulphonic acid by potash-fusion (Kade). Plates or needles, almost

msol cold water Does not give a dys stuff on oxidation (Heumann a Wiernik, B 20, 914)

Di-oxy-di-phenyl-ethane CH, CH(C,H,OH), Ethylidene diphenol [122] (F), [125] (Claus, B 19, 3004) Formed by the action of SnCl, or HCl on a mixture of phenol and paraldehyde (Fabinyi, B 11, 283) Needles (containing c.H.) Reduces ammoniacal AgNO, forming

Di benzoyl derivative [152°] Prisms. Di methyl derivative [140°] Formed from acetyl chloride, anisole, and AlCl, (Gatter mann, B 22, 1129) Micaceous scales

Diethyl derivative [142°] Scales. Isomerides v DI OXY ETHYL-BENZENE.

Tri oxy-tri phenyl-ethane

C_cH₄(OH) CH₂ CH(O_cH₄OH)_x Ethenyl-tryphenol. Formed from CH₂Cl CHCl(OEt) and phenol (Wishcenus, A 243, 153) Amorphous resin, v. sl sol ether Yields iso rosolic acid on oxida tion with FeCl. Forms a tri acetyl derivative.

Tetra oxy di-phenyl ethane

C_sH₄(OH) CH(OH) CH(OH) C_sH₄(OH) Anhydride C₁₄H₁₀O₂. Two isomerides Anhydride C₁₄H₁₀O₂. Two isomerides [68°] and [117°] are formed by the action of zinc dust and HOAc on o oxy benzoic aldehyde (Tiemann, B 24, 3172, Harries, B 24, 3175)

Tetra oxy-tetra-phenyl ethane C20H18(OH) [248°] Formed by fusing tetra phenyl-ethane tetra sulphonic acid with potash (Engler, B 11 930) Plates (from dilute alcohol)

Tetra oxy-tetra-phenyl ethané

(HO C_sH_s)₂CH CH(C_sH_sOH)₂. Formed from droxy benzopherione (Baeyer, A 202, 133) Resun, yielding a crystalline tetra acetyl derivative

Hexa oxy tri phenyl ethane (HO)₂C₆H₃.CH₂.CH(C₆H₃(OH)₂)₂. Three amorphous isomerides are formed from di-chloro-di-ethyl oxide by the action of pyrocatechin, resoroin, and hydroquinone respectively (Wishoenus, A. 243, 181) They are v sol alcohol.

OXY DI PHENYL ETHANE CARBOXYLIC ACID C₄H₄(OH) CH₂ CHPh CO₂H [120° Formed from phenyl-coumarin, dilute alcohol and sodium amalgam (Sardo, G 13, 273) Small

prisms - AgA' sl sol hot water

Oxy-d1-phenyl ethane dicarboxylic acid C_sH₄(CO₂H) CH₂·CH(OH) C_sH₄ CO₂H Hydrooxy-diphthalyhe acid [c. 170°]. Formed from its anhydride, which is a product of the action of zinc-dust and HOAc on phthalic anhydride (Wishicenus, B 17, 2181) Prisms -- AgaA"; decomposes at 225° in vacuo (Hasselbach, A. 243, 249)

Ethyl ether Et.A" Crystalline

Anhydride C₁₆H₁₂O₄ Hydrodiphthallactonic acid [1985°] Prisms. Converted by KCy at 215° into C₆H₄(CO₂H) CH CH.C₆H₄ CO₂H.—

Di-oxy-di-phenyl-ethane di-o-carboxylic acid C.H. (CO.H) CH(OH) CH(OH) C.H. CO.H. Formed by dissolving hydrodiphthalyl in KOHAq (Hasselbach, A 243, 266) Hydrodiphthalyl is a product of the action of zinc-dust and HOAc on diphthalyl The free acid is unstable, at once yielding the anhydride CieHi2Os, which on heating to 190° yields its second anhydride hydrodiphthalyl C₁H₁₀O₂ [250°]—Ag₂A" Pp
Di-oxy-di-phenyl-ethane di-p-carboxylic seid
C₂H₄(CO₂H) CH(OH) CH(OH) C₂H₄ CO₂H

Formed by reducing benzoin dicarboxylic acid

with sodium-amalgam (Oppenheimer, B 19, 1817). M sol water Infusible

O-OXY-PHENYL-ETHYL-AMIDO-ACETIC

ACID Ethyl derivative

C.H. (OEt) NEt CH. CO.H. Formed from chloroacetic and (1 mol), C.H. (OEt) NHEt (2 mols),
and alcohol (Vater, J pr [2] 29, 296) Oil—
Cl. H., NO. HCl. Very hygroscopic—Ethylochloride Cl. H., NO. Etcl. Formed from C.H. (OEt) NEt, and chloro acetic acid (O,2H, NO,EtCl), PtCl, yellow crystals Oil -

p-OXY-PHENYL ETHYLAMINE

C.H. (OH) CH, CH, NH, Formed by heating tyrosine at 270° (Schmitt a Nasse, A 133, 214) Solid. Yields p oxy benzoic acid on fusion with potash (Barth, A 152, 101) -B'HCl Needles

Oxy di-phenyl ethylamine CHPh(OH) CHPh(NH₂) [16 [161°] Formed by reducing the oxim of hydrobenzoin or the mono oxim of benzoin with sodium amalgam and alcohol (Goldschmidt a Polonowska, B 20, 492, 21,488) Needles (from alcohol) —B'HCl [210°] -B',H,PtCl, 2aq —B'HOAc [156°] Di-acetyl derivative [159°] Prisms

p-Oxy-d1-phenyl-ethyl-amine $ilde{E} \, thy \, l \, ether$ EtN(C₆H₅)(C₆H₄ OEt) (319°) Formed from p-oxy-diphenylamine, EtI, and alcoholic potash Oil, with an odour between that of geraniums and violets (Philip a Calm, B 17, 2434)

 β -OXY- β PHENYL-ETHYL ISOAMYL LONIC ACID CHPh(OH) CH2 C(CO2H)2.C4H11 Formed by reducing phenacyl isoamyl-malonic acid with sodium amalgam (Paal a T Hoff mann, B 23, 1503) Thick oil, almost insol water, yielding the lactone of γ oxy γ phenylheptoic acid on distillation

OXY PHENYL ETHYL CARBAMIC ANHY-DRIDE C.H. < NEt > CO [29°] Formed from

C₆H₄ CO, alcoholic potash, and EtI (Bender, B 19, 2952) Not affected by HCl

o - OXY - PHENYL - ETHYL CARBAZIDE O-OXY-PHENYL-ETHYL CARBAZIDE

Methyl derivative $C_{10}H_{15}N_{3}O_{2}$ ie $C_{2}H_{4}(OMe)$ $N_{2}H_{2}$ CO NHEt [110°] Formed

from $C_{6}H_{4}(OMe)$ $N_{2}H_{3}$ and phenyl cyanate

(Reisenegger, A 221, 322) Needles (from Aq)

O-OXY-DI-PHENYL ETHYLENE $C_{14}H_{12}O$ i.e.

C.H. CH CH C.H. (OH) [136°] Formed in small quantity by heating salicylic aldehyde with phenyl acetic acid and NaOAc at 200° (Michael, Am 1, 315) Needles (from alcohol)

p-Oxy-di-phenyl-ethylene Methyl derivative C₁₄H₁₁(OMe) [136°] Formed by heating the methyl derivative of p-coumanc acid (Oglia-

loro, G 9, 536) Plates, sol alcohol Di-o-oxy-di-phenyl ethylene

C₆**H**₄(**OH**) **CH CH C**₆**H**₄**OH** [95°] Formed from salicylic aldehyde, zinc-dust, and HOAc (Harries, B 24, 8178, Tiemann, B 24, 3175) Its alkaline solutions show blue fluorescence Yields a di-benzoyl derivative [108°] which forms a dibromide [59°

Di-p-oxy-di-phenyl-ethylene

C_sH₄(OH) CH CH C_sH₄(OH) Di-oxy-stilbene.

[280°]. Formed by boiling an alcoholic solution of CCl_s CH(C_sH₄ OH)₂ with zinc-dust (E ter Meer, B 7, 1200, Elbs a Hoermann, J pr.

[2] 39, 498) Small crystals (from HOAc)

Yields a di acetyl derivative [218°].

Di-oxy-di-phenyl ethylene Di bensoyl derivative C.H. C(OBz) C(OBz) C.H. Isobenzil [159°] Formed by the action of sodium on a mixture of benzoic aldehydu and BzCl, or on BzCl alone, in ether (Klinger a Schmitz, B 24, 1276) Decomposed by HCl into benzil and benzoic acid Alcoholic potash forms benzoin

Di p oxy di phenyl ethylene Di methyl derivative CH, C(C_eH, OMe)₂ [140°] Formed from anisole, AcCl, and AlCl₂ (Gattermann, B Plates, v sl sol cold alcohol

Yields CO(C_sH₂OM₂, on oxidation by CrO_s
Di-ethyl derivative CH₂C(C_sH₂OEt)
[142°] Formed from C_sH₃OEt, AcCl, and AlCl_s.

Tetra oxy tetra-phenyl ethylene C26H200 Formed by potash fusion from tetra phenylethylene tetra sulphonic acid (Behr, B 5, 278)
Plates (from HOAc) Not melted at 300° FeCl, in HOAc forms green metallic crystals of

C₂₆H₁₆O, laq, sl sol alcohol DI OXY-DI-PHENYL ETHYLENE DIAMINE Di ethyl derivative C2H4(NH C6H4OEt) [98°] Formed by the action of ethylene bromide and Na₂CO₃ on the hydrochloride of C₆H₄(OEt)NH, (Bischoff, B 23, 1979) Plates (from ether alcohol

OXÝ-DI PHENYL-ETHYLENE CARBOXY LIC ACID C₆H₅ CH₂ CH(OH) C₆H₄ CO₂H [96°] Formed from deoxybenzoin o carboxylic acid by sodium amalgam (Gabriel a Michael, B 11, 1020, 18, 3480) Plates (from dilute alcohol) At 100° it forms an anhydride C₁₅H₁₂O₂ [60°]

The isomeric acid

 C_6H_5 CH(OH) CH_2 C_6H_4 CO_2H , [127°], formed by reducing the isomeric deoxybenzoin o carboxylic

acid, also yields an anhydride C_1 , H_1 , O_2 [90°] p OXY-PHENYLETHYLENE - QUINOLINE C,NH, CH CH C,H,OH [253°] Formed from $(Py \ 1)$ quinoline (lepidine) by heating with p oxy benzoic aldehyde and KHSO, at 160° (Hey man a Koenigs, B 21, 1424) Crystals, sì sol dilute NaOHAq

p OXY PHENYL ETHYL KETONE

C₀H₄(OH) CO C₁H₅ Proposely phenol [148°]

S 034 at 15°, 3 3 at 100° Formed by heating phenol with propionic acid and ZnCl₂ (Gold zweig, J pr [2] 43, 86), and also by the action of propionyl chloride on phenol (Perkin, C / 55, 546) Needles or prisms, v e sol alco iol Potash fusion yields phenol and p oxy benzoic acid Yields a di bromo derivative [100°] and a nitro derivative [180°]

Methyl derivative C₈H₄(OMe) CO C₂H₅
[27°] (274°) Formed from anisole (10 g), propionyl chloride (10 g), and AlCl₁ (12 g) in CS₂ (Gattermann, B 23, 1203) Yields an oxim [67°] crystallising from alcohol

Ethyl derivative [30°] Prisms Yields

an oxim C_aH₄(OEt) C(NOH) Et [97°]
D1- oxy-phenyl ethyl ketone

[1 3 4] C₆H₃(OH) CO C₂H₅ [95°] Formed from resorcin (1 pt), propionic acid (1 pt), and ZnCl, (Goldzweig) Needles Gives a red colour with FeCl. Yields a phenyl-hydrazide [115°

Dr-ethyl derrvative C₂H₂(OEt)₂ CO C₂H₃ [76°] Formed from propionyl chloride, C₂H₄(OEt)₂, and AlCl₃ (Gattermann). Yields an oxim [183°] crystallising in needles

Di-oxy-phenyl ethyl ketone

[5 2 1] C₆H₂(OH)₂ CO C₂H₂ [92°] Formed from hydroquinone (1 pt), propionic acid (1 pt.), and

0

ZnCl. (2 pts) at 190° (Goldzweig) Needles, giving a yellowish red colour with FeCl. Yields a phenyl hydrazide [100°]

OXY DI-PHENYL ETHYL NITRITE

C₁₄H₁₈NO₈ te CPh₂(OH) CH₂ O NO [106°] Formed from di phenyl ethane (1 pt), HOAo (10 pts), and HNO₈ (1 pt of S G 1 5) in the cold (Anschutz a Romig, A 233, 327) Needles. oxidised by CrO, to benzophenone and di-phenylvinyl nitrite [87°]

DI OXY DI PHENYL-DI-ETHYL PYRAZ. DIHYDRIDE NPh CHEt CO NPh

[260°] Formed, together with an isomeride [163°], by the action of Ac2O on a phenylamido butyric acid (Nastvogel, B 22, 1795, 23, 2014) Needles (from alcohol)

OXY-PHENYL ETHYL PYRIMIDINE

 $_{\text{CEt}} \!\!\!\! < \!\!\!\! \stackrel{\mathbf{N}-\mathrm{CPh}}{\sim} \!\!\!\! > \!\!\!\! \mathrm{CH}$ $[238^{\circ}]$ Formed from propionamidine hydrochloride, benzoyl aceto acetic ether, and dilute (10 pc) NaOHAq (Pin ner, B 22, 1621) Needles, v sl sol water

OXY TRI-PHENYL ETHYL PYRROLE

CPh₂<CH CPh CO NEt [123°] and [129°] Formed from C₆H₅ CBz CHBz and alcoholic ethylamine (Japp a Klingemann, C J 57, 705) Formed also by heating the ethylamide of di phenyl-Triclinic benzoyl propionic acid at 340° prisms [123°], $a \ b \ c = 912 \ 1 \ 952$, $a = 78^{\circ} \ 48'$, $\beta = 89^{\circ} \ 10'$, $\gamma = 68^{\circ} \ 2'$ From dilute solutions it also crystallises in monoclinic prisms [129°], $a \ b \ c = 1 \ 690 \ 11 \ 958$, $\beta = 86^{\circ} \ 54'$ (Tutton, $C \ J$ 57,731) Yields a biomo derivative C₁₁H₂₀BrNO [142°] crystallising in monoclinic prisms

OXY PHENYL $(Py \ 1)$ ETHYL QUINOLINE $C_eH_4 < C(CH_2CH_2C_4H_4OH) > C_eH_4 < CH_2CH_4OH)$ Formed by con

densing o oxy benzoic aldehyde with (Py 1)methyl quinoline and reducing the product with HI in HOAc and P (Koenigs, B 21, 1428, 2167) The o compound melts at 181°, the m compound at 209°, and the p compound at 177° yield the oxybenzoic acids on fusion with petash

BOXY PHENYL ETHYL SUCCINIC CO.H CHPh CH(CO.H) CH(OH)Me Formed from phenyl acetosuccinic ether, alcohol and sodium amalgam (Weltner, B 18, 791) free acid splits up at once, yielding the anhy dride $C_{12}H_{12}O_4$ [167 5°] whence $C_3(C_{12}H_{11}O_4)_r$ Ag $C_{12}H_{12}O_3$ flocculent pp

AgC, H; O; flocculent pp DI OXY DI PHENYL ETHYL \(\psi\) THIO

UREA Di methyl derivative C.H. (OMe) N C(SEt) NH C.H. OMe [83°] Got from di anisyl thio-urea and EtI (Foerster, B 21. 1863) Prisms —C₁,H₂₀N₂SO₂HI [163°] Rhombohedra —B' H.PtC

O OXY PHENYL GLYCIDIC ACID

C.H.(OH) ĆH ČH CO.H Salicylglycidic acid Formed by the action of cone aqueous NaOH NBz

ĆH ČH OH CO CO benzoyl ımıdo-cumarın upon (Plochl a Wolfrum, B 18, 1185) Flat needles V sol alcohol and ether, sl sol or prisms sold water. By boiling with dilute H.SO, it is con-

verted into oxido-cumarin C₆H₄ CH CH [158°].

-CaA', 6aq prisms o OXY-PHENYL-GLYOXYLIC ACID

CaH. (OH) CO CO2H [44°] Formed by adding acid to a solution of NaNO2 and isatin in dilute NaOH, and heating the solution of the diazo compound thus obtained to 60° (Baeyer a Fritsch, B 17, 973) Yields oa di oxy phenyl acetic acid on reduction with sodium amalgam

Di-oxy-phenyl-glyoxylic acid Methul derivative [431]C.H.(OH)(OMe) CO CO.H. A product of the oxidation of acetyl eugenol by KMnO, (Tiemann, B 24, 2878) Dimethyl Prisms, v sol water and alcohol derivative [4 3 1] CeH₃(OMe), CO CO₂H [139°] Formed, together with veratric acid by oxidation of the methyl derivative of eugenol or isoeugenol by KMnO, (Tiemann a Matsmoto, B 11, 141, Ciamician a Silber, B 23, 1165) Trimetric tables, melting at 100° when hydrated.

Methylene derivative

 $CH_2 < 0 > C_0H_1 CO CO_2H$ [149°] Formed by oxidising iso safrol with alkaline KMnO, (C a S) Light yellow needles, containing benzene of crystallisation (from benzene) —C.H.AgO.

C₅H₄(OH) C₅H₈ CO₂H Anhydride C₁₂H₁ O₂ [54°] (301°) Formed by boiling sodium salicylic aldehyde with valeric anhydride (Perkin, A 147, 235) Prisms (from alcohol), insol cold Aq

An isomeric lactone, prepared by heating phenyl acetyl butyric acid, is oily (Erdmann, 4 254, 182)

OXY PHENYL HEXOIC ACID

CHMe(OH) CH(CH₂Ph) CH₂CO₂H [76°] Small prisms (containing aq) - CaA', 6aq minute prisms Anhydride C, H,O2. Benzyl valero [86°] Formed by reducing benzylacetylpropionic acid with sodium amalgam (Lrdmann, A 254, 182) Crystals (from CS2)

O-OXY-PHENYL-HYDRAZINE Methyl derivative C.H. (OMe) NH NH. [43°] (240°) By reducing C.H. (OMe) N. SO. Na with Zn and glacial acetic acid there is formed the salt CeH4(OMe) N2H2SO, Na aq, which is then warmed with HClAq (Reisenegger, A 221, 314) Needles Yields B'HCl, B',H,C,O,, and (from ligroin) B'C,H,N,O,

Acetyl derivative C, H, N,O, [125°] D1-0 oxy-d1-phenyl hydrasine derivative {C_eH₄(OEt)}₂N₂H₂ [89°] Formed by reducing the azo-compound N₂(C_eH₄OEt)₂ by alcoholic ammonium sulphide (Schmitt a Möh lau, J pr [2] 18, 202) Colourless needles, in sol water, sol alcohol and ether The m 180 meride forms colourless needles [85°] (Buchstab J pr [2] 29, 300)

Tetra - oxy - diphenyl - hydrazine Tetra methyl derivative

C.H. (OMe). NH NH C.H. (OMe). Hydrazodi-methylhydroquinone Formed by reducing the di methyl derivative of nitro-hydro quinone in alkaline solution (Baessler, B 17, 2126) Con verted by acids into the tetra methyl derivative of tetra oxy-diamido-diphenyl

p-OXY PHENYL IMIDO DIACETIC Diethyl derivative of the oxy anilide C₆H₄(OEt) N(CH₂ CO₂H) CH₂ CO NH C₆H₄ OEt [157°] Got from C.H. (OEt) NH CH. CO.H by heating at 260° (Bischoff a Nastvogel, B 22,

00) Crystalline, insol hot water DI-0-0XY-DI-PHENYL-IMIDO ACETO-NITRILE Di-methyl derivative C18H17N2O2 s.s. NH(CHCy C.H., OMe). [123°] Formed by heating C.H. (OMe) CH(OH) CN with alcoholic NH, at 70° (Voswinckel, B 15, 2025) Tables, insol water, sol alcohol

o-OXY - PHENYL - αβ - IMIDO - PROPIONIC ANHYDRIDE Dr-benzoyl derivative {C.H.(OH) C.H.(NBz) CO},O Obtained by heating hippuric soid with salicylic aldehyde dissolved in acetic anhydride with addition of sodium acetate (Plöchl a Wolfrum, B 18,1183) [160°] Crystalline solid By boiling its acetic acid solution with a few drops of aqueous HCl it is converted into the benzoyl derivative of ımidocoumarın

DI-0-0XY-DI-PHENYL IMIDO THIAZOLE Tetrahydride of the di-methyl deriva tive CH₂ < N(C₆H₄OMe) > C N C₆H₄OMe [128°]

Formed by boiling di-anisyl thio urea with C₂H₄Br₂ (Foerster, B 21, 1864) Prisms On heating with CS2 at 200° it yields the compound

 $\begin{array}{c} \text{CH}_2 < \stackrel{\text{N(C,H,O)}}{\text{CH}_2} > \text{CS} \ [136^\circ] - \text{B'}_2\text{H}_2\text{PtCl}_4 \end{array}$

stable when mosst

p-OXY-PHENYL INDAZOLE

 $C^{\circ}H^{\circ} <_N^{CH} > N C^{\circ}H^{\circ} OH$ [195°] Formed by boiling its ethyl derivative with HIAq and a little P (Paal, B 24, 965) Groups of short prisms, v sol HClAq, sl sol ether—B'HI [200°] Large yellow plates

Ethyl derivative [118°] Formed by heating a cone alcoholic solution of the ethyl derivative of o nitro benzyl p amido phenol with tin and HCl Pearly plates (from alcohol), prisms (from benzene ligroin), or needles (from dilute HOAc) The tin double salt crystallises

in yellowish plates [138°] OXY-PHENYL-INDOLE O''H''NO CoH₄COH_{NH}CPh(?) [c 163°] Formed by heating the phenyl hydrazide of ∞ oxy aceto phenone with ZnCl₂ at 160° (Laubmann, A 243,

i) Amorphous pp, v sl sol ligroïn
DI-OXY-DI-PHENYL KETONE v DI-OXY-BENZOPHENONE

D1-oxy-di phenyl-diketone Dr - methyl derivative v AnisiL Anisil forms a monooxim [130°] and two di oxims [195°] and [217°] The (a)-dioxim [217°] forms a diacetyl derivative [189°], while the (β) dioxim [195°] forms an isomeric di acetyl derivative [130°] (Stierlin, B

o-OXY-PHENYL MERCAPTAN

C.H.(SH)(OH) Thropyrocatechin [6°] (217° cor) S G § 1 287, \$\frac{100}{100}\$ 1 189 Formed by reducing di oxy-di-phenyl disulphide with sodiumamalgam (Haitinger, M 4, 170) Formed also by the action of potassium xanthate on diazophenol chloride, the oxyphenyl ethyl xanthate being subsequently saponified by sodium sulphide (Leuckart, J pr [2] 41, 192) Oil, volatile with steam, sl sol water Attacks the skin p-0xy-phenyl mercaptan C₂H₄(SH)(OH) [80°]. (168°) Formed in like manner from

p-diazophenol (L) Crystalline mass, forming a bluish green solution in sulphuric acid -Pb(S C.H. OH), bulky yellow pp Oxidised in alcoholic ammoniacal solution by air to di p-oxydı phenyl dısulphide [151°]

OaH (SH)(CAc) Acetyl derivative (280°)

Di acetyl derivative [66°] Plates Ethyl ethers C.H.(SH)(OEt), [41°], (277°) and C.H.(SEt)(OH), [41°], (287°) Crystalline

OXY-PHENYL METHACRYLIC ACID 18 de scribed as Oxy-phenyl crotonic acid $(q \ v)$

OXY DI-PHENYL-METHANE v BENZYL-

o Oxy tri-phenyl-methane CHPh2.C6H4OH Formed by passing air through a solution of diazoamido tri-phenol methane sulphate, and boiling the product in a current of CO₂ (O Fischer, A 241, 362) Sol alcohol and ether Di p oxy di phenyl-methane CH₂(C₂H₄ OH),

[158°] Formed by fusing di phenyl methane disulphonic acid with potash (Beck, A 194, 318) Plates or needles (from hot water), not volatile with steam Its sodium salts C₁₃H₁₁NaO₂ and $C_{13}H_{10}Na_2O_2$ form green solutions —BaA'

Di-acetyl derivative [70°] Piisms Di-bensoyl derivative [156°] Di methyl derivative CH₂(C₅H₄ OMe)₂ [52°] (M), [49°] (B) (335°) Formed from anisole, methylal, HOAc, and H₂SO₄ (Ter Meer,

B 7, 1200) Small plates (from alcohol)

Di-ethyl derivative CH2(C6H, OEt)2. [39°] Scales, v sol alcohol

Isomeride v Oxy DI PHENYL CARBINOL Di p-oxy tri-phenyl methane

OHPh(O,H,OH)₂ Leucobenzaurn [161°] Formed from di oxy tri phenyl carbinol, zincdust and HCl (Doebner, B 12, 1462, A 217, 230) Formed also from di amido tri phenyl methane by the diazo reaction (O Fischer, A 206, 153), and from benzoic aldehyde, phenol, and H₂SO₄ (Russanoff, B 22, 1943) Yellowish needles (from dilute alcohol), sl sol hot water Absorbs atmospheric oxygen when heated above 160°, changing to dioxy tri phenyl carbinol Potash fusion gives di oxy benzophenone Yields a di nitro compound [134°]

Dr-acetyl derivative [111°] Di-benzoyl derivative [130°]

Tri oxy tri phenyl methane CH(C_cH₄OH), Leucaurin Formed by reducing tri oxy tri-phenyl carbinol (aurin) with zinc dust and NaOHAq (Dale a Schorlemmer, A 166, 286) Colourless prisms (from HOAc), sl sol water

Tri acetyl derivative [139°] (Zulkowsky, A 202, 197) Small needles Tri-benzoyl derivative Small needles

Crystals Tetra-oxy di-phenyl methane? C,,H,2O Formed by fusing orein with NaOH (Barth, M Needles, turning brown at 260° 8, 646)

Tetra-oxy tri phenyl methane $O_{19}H_{10}O_4$ te CHPh($O_1H_1(OH)_2$ [171°] Formed by reducing the anhydride of the corresponding carbinol (resorcinbenzein') with zinc dust and HCl Doebner, A 217, 236) Colourless needles (from Reoxidised by dilute alcohol) alkalıne K.FeCy, to the anhydride of the carbinol

Methyl Octo - oxy - tri - phenyl - methane derivative C.H.(OMe)(OH) OH(O.H.(OH).).
Formed from vanillin (1 pt), pyrogallol (1 67 pts). alcohol (20 pts), and conc HClAq (50 pts.) (Etti,

M 3, 638). Colourless crystals, insol water. turned violet by HCl An isomeride is formed

from vanillin and phloroglucin
p-OXY DI PRENYL-METHANE o-CARB-OXÝLIC ACID Methylderivative reduction of C.H. (OMe) CO C.H. (CO.H. (Nourrisson, B 19, 2105) White needles, insol Aq
Oxy di phenyl methane carboxylic acid

 C_6H_5 CH_2 C_6H_3 OH OO_2H [140°] Formed from sodium benzyl phenol and CO, (Paterno a Fileti, J 1873, 440) Small needles (from water)

-AgA' small needles (from water)
Oxy di phonyl-methane di carboxylic acid CH(OH)(C.H. CO.H). Formed, as K salt, by heating 'diphthalylic acid' with KOHAq at 130° (Juillard, C C 1887, 1143) The free acid at once forms the lactone [205°] which yields a methyl ether [155°], an ethyl ether [995°], and an amide [160°]

Oxy-di phenyl methane tri carboxylıc acıd $C(OH)(C_0H_1CO_2H)$ CO_2H Formed, as K salt, by heating 'diphthalylic' acid C,O2(C,H,CO2H)2 with KOHAq at 110° (Juillard) The free acid changes to lactone

Ethyl ether [108°]

Oxy tri phenyl methane carboxylic acid C,H,O, te CHPh(C,H,OH) C,H, CO,H [210°] Formed by reducing an alkaline solution of oxy tri phenyl carbinol carboxylic anhydride with powdered zinc (Pechmann, B 13, 1616) Needles

Di oxy-tri phenyl methane carboxylic acid C,H,(OH),CHPh C,H, CO,H [184°] Formed by reduction of di oxy tri phenyl carbinol carb oxylic anhydride with zinc dust and NH,Aq (Pechmann, B 14, 1859) Converted into anthranol by H2SO,

Di oxy tri phenyl methane carboxylic acid CH,(CO,H) CH(C,H,OH), [225] Formed by boiling phenol phthalem with zinc dust and NaOHAq (Baeyer, A 202, 80, 212, 350)

Di acetyl derivative [146°] Needles Anhydride CoH, O, [214°-217°] Formed by reducing phenol phthalein anhydride with zinc dust and alcoholic NaOH Small needles (from alcohol) Warm H₂SO₄ forms a green solution turning red

OXY-PHENYL PENTAMETHENYL HY DRIDE v PHENYL METHYL FURFURINE

OXY DI PHENYL DI METHYL DI AMIDO-

BUTYRIC ACID Lactone

O < C(NMePh)2 CH, Phonyl methyl succemide CH, [157°] Got by heating succinic acid with phenyl - methyl - amine (Piutti, G 16, 160) Needles or prisms, sl sol ether

p OXY-DI PHENYL-METHYL AMINE Methyl derivative MeN(C,H,)(C,H,OMe) (313°) Formed by methylation of p oxy diphenyl amine (Philip a. Calm, B 17, 2433)

G:1, with an odour like geranium or violets
ONY DI PHENYL TETRAMETHYLENE. QUINONE (so-called) C16H10O2 The following derivatives of this body are formed by the action of bases on the quinone $C_{10}H_{10}O_2$ got by oxidising di-phenyl butinene (Zincke a Breuer, B. 18, 631, A 226, 88)

Imade $O_{16}H_{\bullet}(OH) < \stackrel{Q}{NH}$. [174°]. plates, yielding a diacetyl derivative [201°] Aqueous SO, forms $C_{zz}H_{zz}O_{z}$ [187°] Methylimide C16H2(OH) [170°]. Ethylimide [130°] Brown needles Phenylimide C₁₆H₂(OH)O(NPh) [158°], o-Tolylimide [108°] Red needles p-Tolylimide [155°] Violet needles

(a) - Naphthy limids [180] Yiolet needles
(a) - Naphthy limids [1480]
Isomeride C₁₀H₁₀(OH)O₂ [1440] Formed by
warming the quinone C₁₀H₁₀O₂ with dilute
NaOH (Z a B) Needles or prisms (from
alcohol) Yields phthalic and on oxidation
Aqueous SO₂ yields an oxyquinhydrone [1550]. HI reduces it to an oxyhydroquinone [73°] -Ca(C₁₆H₉O₂)₂ —BaA'₂ — AgA' brownish-red pp A cety l derivative C₁₈H₁₂O₄ [111°] Benzoy l derivative Monoclinic crystals

DI OXY-DI-PHENYL TRI-METHYLENE ↓ THIO UREA Di-methyl derivative CH₂CH₂N C₆H₄ OMe CH₂S—CN C₆H₄OMe [114°] Formed from di anisyl thio urea and trimethylene bromide (Foerster, B 21, 1872) Prisms (from alcohol)

DI - OXY - DI - PHENYL - DI - METHYL -ETHYLENE DIPYRAZOLE C2H2N,O2 && NPh CO CH CH2 CH2 CH CO NPh Formed by splitting off alcohol (2 mols) from the phenylhydrazide of di acetyl-adipic ether (Perkin a. Obrembsky, B 19, 2049, C J 57, 206) Small crystals, solid at 250° Sol acids and alkalis

OXY-PHENYL-METHYL ETHYL-PYRAZ-OLE $C_{12}H_{14}N_2O$ s.e NPh $<_N^{CO}CMe^{CHEt}$ Formed by heating ethyl acetoacetic ether with phenyl hydrazine at 140° (Knorr a Blank, B 17, 2051) Crystals (containing aq) Oxidised by nitrous acid to C.,H_{2s}N₄O₂ [160°] OXY - PHENYL - METHYL-ETHYL-PYRIM-

IDINE CPh \(\bigcap \) N CMe N C(OH) CEt [167°] Formed from benzamidine hydrochloride, ethylacetoacetic ether, and dilute (10 pc) NaOHAq (Pinner, B 22, 1625) Prisms

D1 - oxy - phenyl - methyl - ethyl - pyrimidine Ethyl derivative

 $C_{e}H_{\bullet}(OEt) C \leqslant_{N}^{N} C(OH) \gg CEt.$ [194°] Formed from ethyl-acetoacetic ether and p-ethoxybenz-amidine (Pinner, B 23, 2955) Needles (from amidine (Pinner, B 23, 2955) alcohol), m sol hot alcohol

OXY PHENYL-DIMETHYL-TETRAHYDRO-PYRIDINE v BENZYLIDENE-DIACETONE-ALCAMINE OXY PHENYLMETHYL KETONE v. Oxy-

ACETOPHENONE and BENZYL CARBINOL DI OXY DI-PHENYL-DI-METHYL-PYRAZ-INE DIHYDRIDE NPh CHMe CO NPh

[183°] Formed from phenyl-a-amido propionia acid and Ac_2O in the cold (Nastvogel, B 22,

1794, 23, 2012) Needles, misol water An isomeride [146°] accompanies the preceding body On heating with KOHAq both compounds yield O_{1.}H_{2.}N.O, [80°] OXY-PHENYL-METHYL-PYRAZOLE

 $NPh <_{N=OMe}^{CO CH_2}$ [127°] (287° at 265 mm.).

Preparation .- 1 By heating accordence ther with phenyl hydrazine (Knorr, B 17, 550, 2082; A. 288, 187) -2 By the action of NH, Aq and H2S on (8)-phenyl-azo-crotonic ether (Bender, B 20, 2748)

Properties - Crystals, sol hot alcohol Yields bromo-, dibromo-, and di-chloro- derivatives Condenses with cinnamic aldehyde, acetone, and acetoacetic ether Zinc dust reduces it to Excess of phenylphenyl methyl-pyrazole hydrazine forms, on boiling, C20H18N4O2, whence C20H18N4O2(SO3H)2 Nitrous acid forms C10H2N3O2 [137°] Diazobenzene chloride forms a compound NPh CO C N2HPh [155°], which is also got by heating azobenzene acetoacetic amide with phenyl hydrazine at 130° (Leuckart a Holzapfel, B 22, 1406, Buchka, B 22, 2541) S₂Cl₂ forms a product which crystallises from alcohol as $C_{20}H_{16}N_4SO_2HClHOEt$ (Sprague, C J 59, 334) Alloxan forms a compound $C_{14}H_{12}N_4O_5$, whence dilute potash gives C13H11N3O4, converted by hot potash into C11H12N2O, which on heating with alcohol gives rise to oxy phenyl methyl methyl ene-pyrazole [178°] (Pellizzari, A 255, 230)

Oxy-phenyl-d1-methyl-pyrazole C11H12N2O 1.6 NPh CO CHMe [117°-120°] Formed by heating methyl acetoacetic ether with phenylhydrazine at 140° (Knorr, B 17, 2050, A 238, 162) Formed also by heating oxyphenyl methyl pyrazyl acetic acid Crystalline powder Oxy-phenyl-di-methyl-pyrazole C,1H,2N2O & e

NPh CO-CH NMe CMe Antipyrine [113°] Formed by methylation of oxy-phenyl methyl pyrazole (Knorr, B 17, 2032) and by heating acetoacetic ether with s phenyl methyl-hydrazine (Knorr, A 238, 203) Monoclinic crystals (from water), v sol water, alcohol, and ether Februiuge FeCl, colours its solution deep red Nitrous acid gives a bluish green colour Sodium added to its solution liberates methylamine K₃FeCy₆ and HCl give a yellow colour Chromic acid gives an orange pp (Gay a Fortuné, Ph 18, 1066) Gives the usual reactions for alkaloids ICl solution forms crystalline C₁₁H₁₁IN₂O [160°] and C₁₁H₁₁IN₂OICl [142°] (Dittmar, B 18, 1617) Bromine forms C₁₁H₁₂Br₂N₂O [c 150°], whence water yields C₁₁H₁₁BrN₂O [117°] HNO₂ forms C11H11N3O2, which explodes at 200° Alloxan yields NPh CO NH CO NH CO, decomposing at 261°, whence boiling cone HClAq forms C₁₂H₁₂N₂O₂ [238°] (Pellizzari, G 18, 340) Benzoic aldehyde in presence of HCl forms benzylidene-di antipyrine C29H28N4O2 [201°] Combines with chloral

Salts $-B'_2H_2PtCl_6$ 2aq $-B'_2H_4FeCy_6$ $-B'C_6H_2(NO_2)_9OH$ [188°] Long yellow needles Oxy phenyl tri-methyl-pyrazole C₁₂H₁₄N₂O NPh<CO-CMe [88°] (286° at 153 Formed by heating antipyrine with MeI mm) and MeOH (Knorr) Crystals, v sol water and ohol Yields a picrate [94°]
Oxy-phenyl-tri-methyl-pyrazole alcohol C12H14N2O

ve NPh CO CMe, N=CMe [56°] oxy phenyl methyl pyrazole Formed from NaOMe, and MeI (Knorr, A 238, 165), and also by heating di-methyl-acetoacetic acid with phenyl hydrazine Insol water, v sol alcohol Oxy-di-phenyl-methyl-pyrazole $C_{16}H_{14}N_2O\imath$ e NPh < CO-CH NMe CPh.

[150°] Formed by methyla-

tion of oxy di phenyl pyrazole (Knorr a Klotz, B 20, 2549) Needles (from ether), sl sol boiling water Bromine in chloroform forms a di bromide, whence water liberates CieHisBrN.O [110°-120°]

needles -B'2H,FeCy Salts —B'HCl B'C₆H₂(NO₂)₃OH [170°] Yellow prisms

Oxy di-phenyl methyl pyrazole

NPh CO CH [122°] Formed by heat ing hydrazobenzene with acetoacetic ether at 120°, the yield being 60 pc of the theoretical (Muller, B 19, 1771, Perger, B 19, 2140, M 7, Crystals (containing \(\frac{1}{2} aq \), v sol alcohol

OXY PHENYL METHYL-PYRAZOLE CARB OXYLIC ACID NPh CO CHMe N=C CO,H

Made from its ether, which is got by heating oxal propionic ether with phenyl hydrazine at 120° (Arnold, A 246, 331) Plates (from alcohol) Ethyl ether EtA' [149°]

Oxy phenyl methyl pyrazole carboxylic acid NPh CO CH, CO,H [134°] Got from its ether [85°], which is formed by heating acetone dicarboxylic ether with phenyl hydrazine (Pech mann, A 261, 171) Prisms, sol alcohol

Oxy-phenyl methyl pyrazole dicarboxylic NPh CO (H CH, CO,H Formed by saponifying its ether Needles (con taining aq), sl sol cold water Gives a dark

violet colour with FeCl₃
Ethyl ether Et₂A" [130°] Formed by heating oxalsuccinic ether with phenyl hydraz ine at 170° (Wishcenus, B 22, 888) Needles

Oxy phenyl di methyl pyrazole carboxylic acid NPh CO CH CH2CO2H [178°] Ob tained from its ether [138°], which is got by heat ing acetyl succinic ether with phenyl hydrazine at 150° (Knorr) Needles (from water)

DI OXY-DI PHENYL DI - METHYL DI-PYRAZYL C20H19N4O2 & e NPh CO CH CH CO NPh Formed by the action of phenyl hydrazine (3 mols) on acetoacetic ether (2 mols) Formed also by the action of phenyl hydrazine on di acetyl succinic ether, on isocarbopyrotritaric ether and on thioacetoacetic ether (Knorr, B 17, 2044, 2058, 22, 160, Buchka a Sprague, B 22, Formed also from β phenyl azo crotonic 2554) ether, alcoholic NH, and H₂S (Bender, B 20, 2749) Yellowish powder Decomposes on 2749) Yellowish powder heating without melting Insol neutral sol Gives the pyrazole blue revents, sol alkalıs Yields a bromo derivative [217°]

D1-oxy-d1 phenyl-tetra methyl dipyrazyl $\begin{array}{ccc}
\text{NPh CO} & \text{CMe} \\
\text{N} & \text{CMe}
\end{array}$ Formed by oxidation of oxy phenyl di methyl pyrazole with nitrous acid (Knorr a Blank, B. 17, 2050) Long prisms (from HOAc), insol water and alkalis, sol conc H2SO4

Di-oxy di-phenyl-tetra methyl dipyrasyl NPh CO NMe CMe>C C≪CMe NMe Bis antipyrine [245°] Formed by methylation of the preceding body (Knorr, A 288, 210) Crystals (from MeOH), nearly insol water —B'H₂Cl₂ 2aq —B'₈H₄PtCl₈ orange red prisms Picrate [o 161°]

Di oxy di phenyl di-methyl-dipyrasyl sulphide (NPh CO CH)₂S Formed by adding phenyl hydrazine (2 mols) dissolved in HOAc to thio aceto acetic ether (1 mol) in the cold (Buchka a Sprague, B 23, 849) Formed also from oxy phenyl methyl pyrazole and SCl₂ in chloroform Small needles, decomposing at 183° without melting, al sol alcohol, sol alkalis

OXY PHENYL METHYL PYRIDAZINE

NPh CO CH N CMe CH [82°] Formed, together with its chloro- derivative [137°], from the an hydride of the phenyl hydrazide of levulic acid and PCl, at 160° (Ach, A 253, 47) Translucent crystals, v sol alcohol Na added to its alcoholic solutions forms a compound C₂H₂₁N₄? [200°], coloured violet by H₂SO₄ and CrO₃—B'HCl

Di oxy-phenyl-methyl-pyridazine

 $\begin{array}{lll} {\rm NPh} < \begin{array}{l} {\rm CO \ CO} \\ {\rm N \ CMe} \end{array} > {\rm CH_r} & [196^{\circ}] & {\rm Formed \ from} \\ {\rm the \ chloro \ derivative, mentioned \ above, by \ treat} \\ {\rm ment \ with \ alcoholic \ potash, \ the \ resulting} \\ {\rm NPh} < \begin{array}{l} {\rm CO \ C(OEt)} \\ {\rm N=CMe} \end{array} > {\rm CH \ [146^{\circ}] \ being \ heated \ with} \end{array}$

HClAq at 130° White needles, sl sol hot water OXY v PHENYL-DI METHYL PYRIDINE

C₁₃H₁₃NO is NPh CMe CH CO Phenyl lutidone [197°] (above 360°) Formed by the action of aniline on methyl dehydracetate (Perkin, B 18, 682, C J 51, 498), and also by heating its carboxylic acids (Conrad a Guthzeit, B 20, 161, 22, 85) Needles or prisms (containing aq) v sol hot water and alcohol—B'C₂H₂(NO)₃OH [95°] Transparent plates

Oxy pnenyl di methyl pyridine

NMe CO CH CPh Methyl phenyl \(\psi \) problem lostyril 112° Formed by heating 'methylcarbo phenyl lutidylium dehydride' with conc HClAq at 180° (Hantzsch, B 17, 2915) Prisms [HClQ ac argitallium prowides]

HClAq at 180° (Hantzsch, B 17, 2915) Prisms
B'HCl2aq —B'.H.PtCl, 3aq crystalline powder
m-0xy (Py 3) phenyl (Py 15) di methylpyridine C.,H.,NO 1e C.H. (OH) C,NH. (CH.).
Oxy phenyl luttime [191°] From the corresponding amido compound by the diazoreaction White crystalline solid (Lepetit, B
20, 2399) — B'HCl 2aq —B'.H.PtCl, [c 200°]

OXY " PHENYL DI METHYL PYRIDINE CARBOXYLIC ACID C, H, NO, 16

NPh < CMe CH > CO [257°] Formed by heating the dicarboxylic acid at 227° (Conrad a Guthzeit, B 20, 161, 947, 22, 84) Formed also from β phenyl amido crotonic ether and NaOEt at 90° (Knorr, B 20, 1399) Satiny needles Melts at 267° when quickly heated $-BaA'_2$ 4aq needles, ν sol water

Methyl ether MeA' [152°] Formed from methyl dehydracetate and aniline (Perkin, jun, B 18, 682, C J 51, 498) Needles

Oxy-phenyl-di methyl-pyridine dicarboxylic acid NPh CMe C(CO₂H) CO Got by electrolysis of its ether Prisms, v sol hot alcohol—Ba(HA")₂ aq

Ethyl ether Et.A" [171°] Formed by

boiling an acetic acid solution of aniline and the product of the action of COCI, on cupric acetoacetic ether (Conrad a Guthzeit, B 19, 25, 20, 161) Crystalline solid, v sol alcohol— B'₂H₂PtCl₄ [120°] Orange yellow pp

 $B'_2H_2PtCl_*$ [120°] Orange yellow pp m Oxy-(Py 3) phenyl-(Py 15)-di-methylpyridine-(Py 24) di carboxylic acid $C_6H_4(OH)$ $C_5N(CH_3)_2(CO_2H)_2$. m Oxy phenyl-

 $C_8H_1(OH)$ $C_5N(CH_3)_2(CO_5H)_2$. m Oxy pheny lutrdine di carboxylic acid

Di-ethyl-ether A"Et₂ [174°] From the corresponding amido compound by the diazo reaction (Lepetit, B 20, 2398) White needles OXY PHENYL METHYL PYRIMIDINE

CPh $\stackrel{N \text{ CMe}}{\sim}$ CH₂ [216°] Formed by mixing a solution of benzamidine hydrochloride (1 mol) with acetoacetic ether (1 mol) and NaOH (1 mol) Formed also by the action of benzimido ether CPh(NH) OEt on acetoacetic ether at 100° and of benzamidine on acetyl malonic ether (Pinner, B 18, 759, 2851, 22, 1624, 2617,

23, 3820) Needles, v sol alcohol, sl sol water

—B' H.PtCl, 2aq — B'C, H.(NO), OH [189°]

B' H. Cr.O 5aq [177°] Orange red prisms

Acetyl derivative C₁₂H₁, N.O. [41°]

Acetyl derivative C₁₂H₁₂N₁O₂ [41°] Ethyl derivative C₁₁H₂(OEt)N₂ [31°]. (300°) Formed from chloro phenyl methylpyrimdine and NaOEt Thick prisms — B HCl 2aq [86°] -B'HCl [149°] -B'₂H₂PtCl₆. [197°] -B'HI aq [144°] Yellow prisms

Oxy phenyl methyl pyrimidine

CMe N CPh CH. [238°] Formed from acetamidine hydrochloride, benzoyl acetic ether, and dilute (10 pc) NaOHAq (Pinner, B 22, 1618) Needles, m sol hot alcohol

Oxy phenyl-di-methyl-pyrimidine

CPh N CMe CHMe [203°] Formed from benzamidine hydrochloride, methyl acetoacetic ether, and NaOHAq (Pinner, B 22, 1624) Needles

Oxy di-phenyl-methyl-pyrimidine CPh $\stackrel{N}{\sim}$ N CPh (250°) S 1 95 at 20° Formed from benzamidine and a benzoyl propionic ether (E v Meyer, J pr [2] 39, 197, 40, 303, Schwarze, J pr [2] 42, 12) Minute needles Oxidised by KMeO, to oxy di phenyl pyrimidine carboxylic acid [236°] Yields a methyl derivative $_{1}$ 122°]

Di-oxy-phenyl-methyl-pyrimidine Ethyl derivative $C_oH_o(OE)$ $C < N CMe > CH_o$ [146°] Formed by mixing o ethoxy benzamidine hydro chloride with NaOH and acetoacetic ethei (Pinner, B 23, 2953) Short columns, v sol alcohol

An isomeride [204°] is formed from p ethoxy benzamidine and acetoacetic ether or acetylmalonic ether

Di-oxy-phenyl-di methyl-pyrimidine Ethyl derivative C₂H₄(OEt) C \ll N CM $_{
m CO}$ >CHMe

[216°]. Formed from p ethoxy benzamidine and methyl acetoacetic ether (P) Small prisms

Reference — Bromo - OXY - PHENYL - METHYL

PYRIMIDINE

OXY-PHENYL-DI-METHYL PYRIMIDINE CARBOXYLIC ACID

CPh N CMe CH CH₂ CO₂H [259°] Gos by saponifying its ether Needles, all sol water. Ethyl ether EtA' [178°] Formed from acetyl succinic ether and benzamidine (Pinner B 22, 2618) Crystals, sl sol water

OXY-PHENYL-METHYL-PYRIMIDYLME THYL METHYL KETONE

CPh N CMe C CH₂ CO CH₃ [225°] Formed from di-acetyl-succinic ether and benzamidine (Pinner, B 22, 2622) Needles, sl sol alcohol

OXY-PHENYL-METHYL PYRIMIDYL PRO-PIONIC ACID

 $CPh \leqslant_{NCO}^{N.CMe} > CH CH_2 CH_2 CO_2H$ [215°]

Formed by saponification of its ether [145°], which is got by the action of benzamidine on acetyl glutaric ether (Pinner, B 22, 2620) Powder, sl sol water

OXY-TRI PHENYL-METHYL PYRROLE

C₂H₁₈NO ie NMe<CO CPh. Tri phenylmethyl pyrrholone [139°] and [148°] Formed from C₄H₅ CBz CHBz and alcoholic methylamine (Japp a Klingemann, B 22, 2884, C J 57, 698) Colourless rhombohedra [139°], ac = 12 484 Occurs also in triclinic forms [143°], a b c = 906 1 870, a = 79°52', β = 86° 3', γ = 70° 26' (Tutton, C J 57, 724) Oxidised by chromic acid to C., H₁₈NO, [157°] Bromine in chloroform yields C₂, H₁₈B₂NO [150°]

Oxy-tetra-phenyi-methyl-pyrrole $C_{75}H_{23}NO$ se NMe $\stackrel{\textstyle <CO}{CPh}$ CPh CPh CPh (161°) Formed by heating C_9H , CBz CBz C_9H , with alcoholic methylamine at 200°, and also from benzoyl-triphenyl propiomethylamide and KOH (Klingemann a Laycock, C J 59, 146, B 24, 518) Small yellow monoclinic plates (from boiling

alcohol), v sol CS₂.

OXY-PHENYL METHYL PYRROLE CARB-

OXYLIC ACID Ethyl ether

NH CO CHPh [128°] Formed by the action of alcoholic ammonia on phenyl acetyl-succinic ether (Emery, A 260, 152) Needles

Oxy-phenyl-methyl pyrrole dihydride carbexylic acid NPh $\stackrel{CO}{C}$ Che $_{1}$ Che $_{2}$ Che $_{2}$ Che $_{3}$ Che $_{4}$ Che $_{1}$ Che $_{2}$ Che $_{3}$ Che $_{4}$ Che $_{4}$ Che $_{5}$

Netrele Oil Converted by NH, and H₂S into NPh CO—CH₂ CH₂ [198°] Hydroxylamine forms the amidoxim [120°]

OXY - PHENYL - METHYL - QUINAZOLINE

C_tH. CO NMe [181°] Formed by the action of KOH and MeI at 120° on c-benzoyl amidobenzamide or on oxy phenyl quinazoline (Körner, J pr [2] 86, 162) Shining lamellæ, sol alcohol Isomeride C_sH. CO NPh | [147°]. Formed

by heating the acetyl derivative of o amido benzoic anilide (K) Four-sided prisms

OXY - PHENYL - METHYL - QUINOLINE CMe CH C C(OH) CH CH=CH CN — CPh ing its carboxylic acid at 250° (Just, B 19, 1544) Plates (from alcohol)

Isomeride v Flavenol

OXY - PHENYL - METHYL - QUINOLINE CARBOXYLIC ACID CMe CH C C(OH) C CO₂H CH CH CN — CPh .

Formed by saponifying its ether [236°], which is got by heating to 160° the product of the action of C₆H₁MeN CClPh on sodium malonic ether (Just, B 19, 1542) V sl sol water and alcohol

OXY - PHENYL - METHYL - (Py) - QUINO-

N — NPh

C C C CMe

PYRAZOL C.H. | Inner - anhy-

dride of o amido di phenyl methyl pyrazol-carboxylic acid [261°] Formed by reduction of o nitro di phenyl methyl pyrazol carboxylic acid with SnCl₂ (Knorr a Jödicke, B 18, 2262) Fine needles V sol alcohol, chloroform, and acetic acid, insol water, alkalis, and dilute acids. It can be distilled undecomposed. It is a very stable body. By sodium and alcohol it is reduced to a hydro compound which dissolves in strong H₂SO₄ with a deep green colour.

 $\begin{array}{ccc} \textbf{OXY} & \textbf{PHENYL-METHYL-QUINOXALINE} \\ \textbf{C}_{s}\textbf{H}_{1}\textbf{Me} < & \textbf{N} & \textbf{C(OH)} \\ \textbf{OPh} & \textbf{CPh} & \textbf{Formed from (1,3,4)} \\ \textbf{tolylene diamine} & \textbf{and} & \textbf{phenyl glyoxylic} & \textbf{acid} \\ \textbf{(Hinsberg, A 237, 352)} & \textbf{Pale yellow needles} \end{array}$

γ 0ΧΥ-γ-PHENYL-3 DI-METHYL-SUCCINIC ACID CHPh(OH) CH(CO₂H) CHMe CO₂H Phenyl homo tamalic acid The free acid is unstable, but the salts CaA"3aq, BaA"2aq, and Ag₂A" are got by boiling its lactone with bases (Fittig a Penfield, B 216, 119, 20, 3179)

a Penfeld, B 216, 119, 20, 3179)

Lactone [177°] Phenyl homoparaconic acid Formed from benzoc aldehyde, sodium pyro tartrate, and Ac.0 by heating for 10 hours at 130°

Plates (from water) Yields AgA' Forms phenyl-butylene (177°) on distillation Cone HBr at 0° forms CHPhBr CH(CO₂H) CHMe CO₂H [149°] which on warming with water becomes CHPh CH CHMe CO₂H The lactone [177°] is accompanied by an isomeride [124 5°] The lactone [177°] yields on distillation methylnaphthol [89°], while the isomeride yields an isomerine methyl naphthol [92°] Both methylnaphthols yield (8) methyl naphthalene on distillation with zine dust

o - Oxy - phenyl - di - methyl succinic acid C_eH₄(OH) CH₂CH(CO_.H) CHMe(CO_.H) [145° 150°] Formed by reducing coumaryl propionic acid in alkaline solution with sodium amalgam (Fittig a Brown, A 255, 288) Crystals, v sol water —BaA" — CaA" —Ag₂A" curdy pp

Oxy-phenyl-methyl succinic acid is described as Oxy BENZYL-SUCCINIC ACID

OXY-DI PHENYL-METHYL ψ-THIO UREA.

Methyl derivative

C_cH₄(OMe) NH C(SMe) NPh [80°] Formed by the action of MeI on phenyl anisyl thio urea (Foerster, B 21, 1870) Long white needles

Di oxy-di phenyl-methyl-v thio-urea methyl derivative C.H. (OMe) NH C(SMe) NC.H. OMe [87°] Made by heating di-anisyl thio urea with MeI at 100° (Foerster, B 21, 1860) Prisms, v e sol hot alcohol Yields on distillation MeSH and a substance [56°] which on boiling with dilute HCl gives di anisyl urea [184°] —C₁₈H₁₈N₂SO₂HCl white plates -B'2H2PtCl

ite plates — B'2H2PtCl prisms OXY-PHENYL-NAPHTHYL-ACETIC CPh(C₁₀H₁)(OH) CO₂H The salt NaA' 2aq [145°] is formed from sodium phenyl (a) naph thyl ketone, water, and CO₂ (Beckmann, B 22,

oa DI OXY PHENYL NAPHTHYL KETONE C₆H₄(OH) CO C₁₀H₆(OH) [c 106°] Formed by heating (a) phenonaphthoxanthone with alcoholic potash at 200° (Phomina, A 257, 93) Yields a methyl derivative [66°], an acetyl dernatue [137°] and an acetoxim [196°]

The oß isomeride [169°] yields K,A" and a methyl derivative [68°], an ethyl derivative [c 141°], an acetyl derivative [108°], an acetoxim [188°], and a phenyl hydrazide [198°]

DÍ OXY DI PHENYL OCTANE

CPhPr(OH) CPhPr(OH) [64°] Formed by the action of sodium amalgam on a solution of phenyln propylketone in dilute alcohol (Schmidt Fieberg, B 6, 499) Needles (from acetone)

Di oxy di phenyl-octane C.H. CMe(C.H.OH).

50] Formed from methyl hexyl ketone, phenol, and HCl (Dianin, J R 1888, 534) Needles Yields a di benzoyl derivative [114°] OXY PHENYL OXANTHRANOL C,0H,4O,

 $\bullet e \quad C_6H_1 < \frac{CO}{C(OH)(C_6H_4OH)} > C_6H_4$ [194°] Formed by oxidising ovy phenol anthranol with KMnO₄ (Pechmann B 13, 1617) Yellowish Yields authraquinone on oxidation

Acetyl derivative C, H16O4 Needles Di oxy-phenyl oxanthranol PHTHALIDFIN

OXY PHENYL-ISO OXAZOLE

CPh CH. CO [147°] Formed from benz ovlacetic ether and hydroxylamine in acid, neutral, or ammoniacal solution (Claisen a Zedel, B 24, 141, Hantzsch, B 24, 502) Needles, al sol cold alcohol HClAq at 120° yields the oxim of acetophenone Ammonia forms CPh CH ONH, [168°] Yields a

nitroso derivative $CPh \leqslant_{N O}^{C(NOH)} > CO$ [143°]

DIOXY DI PHENYL OXIDE C12H10O3 2 e O(C₆H₄OH)₂? Formed from phenol and CrO₂Cl₂ (E1 rd, Bl [2] 28, 276) Amorphous powder Yields quinone on oxidation, v Ri sorcis

DI OXY DI PHENYL OXINDOLE C20H15NO. NHCOO C(C.H.OH), Phenolisatin Formed by adding H2SO4 to a mixture of isatin and phenol (Baeyer a Lazarus, B 18, White needles, insol water, sol alkalis Acetyl derivative C20H14O2NAc [185°]

Colourless needles (from HÖAc)

Di methyl derivative C₂₀H₁₁Me₂NO₂.

[65°] Made from anisole, isatin, and H₂SO₄. p oxy-phenyl pentadecyl ketone Methyl derivative C₁₄H₂₁ CO C₄H₄ OMe [70 5°] (280° at 15 mm.) Formed from anisole,

D:- | palmityl chloride, and AlCl. (Krafft, B 21,

> Ethyl derivative [69°] (289 at 15 mm) Formed in like manner from phenetole Plates

Di oxy-phenyl pentadecyl ketone (290° at methyl derivative [635°] (290° at 15 mm) Formed in like manner from the dimethyl derivative of resorcin (K)

DI OXY PHENYL PENTANE CHPh(OH) CH(OH)Pr [82°] (287°) Formed by the action of alcoholic potash on a mixture of benzoic and isobutyric aldehydes (Swoboda, M 11, 390) White crystals, v sol ether

Di-acetyl derivative C15H O4 $(297^{\circ}$

Di oxy phenyl pentane

CHPh(OH) CH, CH, CH, CH, OH Formed by reducing benzoyl butyl alcohol with sodium amalgam The glycol is extracted with ether (Kipping a Perkin, jun, C J 57, 312). Needles (from benzene), v sol ether

Di-oxy-di-phenyl-pentane CEt₂(C,H,OH), Formed from di ethyl ketone, phenol, and HCl (Dianin, J R 1888, 534) On fusion with NaOH it yields C_5H_{11} C_5H_4OH [76 5°] (253°)

OXY PHENYL PENTENOIC ACID v PHENYL ANGELIC ACID

DI OXY DI PHENYL-PENTINOIC ACID

Di methyl derivative C.H.(OMe) CH CH C(CO.H) CH C.H.(OMe [160°] Formed from p methoxy benzoic alde hyde, sodium succinate, and Ac2O (Fittig & Politis, A 255, 299) Long yellow needles (from HOAc)—BaA'₂2aq silky plates—CaA'₂3aq—AgA light yellow pp
OXY-PHENYLENE-ANTHRA.

QUINONE DIHYDRIDE CaH to O 16

C,H (OH) C.H.Ph [266°] Formed by

fusing truxone with potash (Liebermann a Bergami, B 23, 321) Yellow needles, sl sol alcohol Yields an acetyl derivative $C_{28}H_{15}AcO_{8}$ [180°], v sol HOAc

OXY-DI PHENYL PHOSPHINE derivative P(C₆H₃)₂ OPh (265°-270° at 62 mm) SG ²⁴/₄ 114 VD 1002 (obs) Got by heating PPh2Cl with phenol (Michaelis a. La Coste, B 18, 2109) Oil Readily absorbs oxygen from the air, becoming (C₆H₃),PO OPh. Sulphur yields (C₆H₃),PS OPh [124°] Selenium forms Ph₂PSc(OPh) [115°] Yields a crystalline methylo iodide [c 136°] and a benzylo chloride Ph.P(OPh)C,H Cl [232°-236°]

TETRA - OXY - DI PHENYL - PHTHALIDE. Anhydridev Fluorescein

OXY PHENYL-PHTHALIMIDE v. AMIDO-PHENOL

DI-OXY-DI-PHENYL-PROPANE

 $\mathrm{CMe_2(C_0H_1OH)_2}$ [154° cor] Got from acetone, phenol, and BzCl (Dianin, J R 1888, 534) Flat needles Yields, on soda-fusion, p isopropylphenol [61°

OXY PHENYL-PROPIOLIC ACID v Cov-MARILIC ACID

 α -OXY β PHENYL-PROPIONIC ACID

C₅H₅CH₂CH(OH) CO₅H [98°] Formed from phenyl acetic aldehyde, HCy, and HCl (Erlenmeyer, B 18, 308, A 219, 179) Got also by reducing phenyl glycidic acid with sodium-amalgam (Plöchl B 16, 2823) Prisma (from

Yields formic acid and phenyl-acetic acid on heating —BaA'2 aq globular aggregates Netrale [58°] Needles (from benzene)

β Oxy β phenyl propionic acid C,H,CH(OH) CH,.CO,H [93°] Formed by the action of sodium amalgam on the acid C.H. CH(OH) CHCl CO.H (Glaser, A 147, 86) and by boiling \$-bromo \$-phenyl propionic acid with water (Fittig a Binder, A 195, 138) also by reducing benzoyl acetic ether with sodium amalgam (Perkin, C J 47, 254) Prisms, v sol cold water Yields cinnamic acid on heating with baryta water (Kast, A 206, 26) or with dilute H₂SO, at 100° (Erlenmeyer)—KA'—BaA'₂1½aq—ZnA'₂1½aq—AgA' needles

Acetyl derivative [100 5°] Crystals

Yields cinnamic acid when heated with Ac2O at

120° (Slocum, A 227, 59)

β Oxy-α-phenyl-propionic scid CH2(OH) CHPh CO2H Tropic acid Mol w

[118°] S 2 at 145° 166 Formation -1 By decomposing atropine or

hyoscyamine with fuming HClAq or with baryta water (Lossen, A 138, 230, Kraut, A 148, 238, Ladenburg, B 13, 607) —2 From atropic acid by union with HOCl followed by reduction with zinc dust, iron filings, and conc KOHAq (Laden burg a Rugheimer, B 13, 379) -3 From atropic acid by heating it with fuming hydrogen chloride at 100° and digesting the resulting acid (CH Cl CHPh CO H) with aqueous Na₂CO, at 120° (Ladenburg, A 217, 114) —4 From aceto phenone cyanhydrin by treatment with HCl, the resulting chloro phenyl propionic acid being heated with sodium carbonate (Spiegel, B 14, 237, 1352, Merling, A 209, 5)

Properties - Needles or tables, v sol water Yields phenyl acetic acid on fusion with potash Chromic mixture oxidises it to benzoic acid

Salts - CaA'2 4aq -AgA' crystals Reference -CHLORO TROPIC ACID

a Oxy a phenyl propionic acid

C_eH, CMe(OH) CO₂H Atrolactic acid [94°] Formation -1 From atropic acid by successive treatment with HBr and aqueous Na2CO3 (Fittig a Wurster, A 195, 145, 206, 24) -2 By oxidation of a-phenyl propionic acid with al kalıne KMnO, (Ladenburg a Rugheimer, B 13, 373, A 217, 107) -3 By reduction of the dibromo derivative obtained by the action of H2SO, on a mixture of dibromo pyruvic acid and benzene (Böttinger, B 14, 1238) -4 By dissolving the cyanhydrin of acetophenone in saturated HClAq (Spiegel, B 14, 1353, Tiemann, B 14, 1980)

Properties -Trimetric needles or tables (containing aq), a b c = 72 1 57 Becomes anhydrous below 85° Gives rise to atropic acid Salts —CaA', 8aq —BaA', 2aq —ZnA', 2aq.

small crystals, v sl sol cold water

Ethyl derivative CMePh(OEt) CO2H 'Ethyl tropic acid' [c 62°] Formed from acetophenone by treatment with PCl, acting upon the resulting Ph CCl, Me with KCy and dilute alcohol, and saponifying the product with baryta Small prisms, sol hot water

Nutrule Formed from acetophenone, KCy

and HCl (8) Oıl

Formed from phloretin (7g) and KOH (55 c.c. of SG 12) by boiling for 3 hours (Hlasiwetz, J 1855, 700, Schiff, A 172, 357) Formed also from amido phenyl propionit acid by diazo re action (Trinius, A 227, 268) Yellowish reedles V sol hot water, sol alcohol and ether, insol CS₂ Yields p oxy benzoic acid on fusion with potash On heating with phloroglucin at 180° it yields the crystalline phloroglucide Css HwO14 Heating with POCl, forms crystalline triphlo retide $C_{27}H_{26}O_7$ Phloretic acid gives a green

colour with FeCl₂, possibly due to phloroglucin Salts—BaA'₂ 2aq—CuA'₂ (at 120°) Ethyl ether EtA' (above 205°) Isoamyl ether C, H, A' (above 290°) Methyl derivative

 $C_6H_4(OMe)$ CHMe CO_2H [103°] S 11 at 25. Got by methylation (Körner a Corbetta, B 7, 1732) Yields BaA', 2aq and MeA' [38°] (278°) Ethyl derivative [106 5°] Scales

Amide C.H., NO. [110°-115°] Isophloretic acid, made by boiling isophlo retin with KOHAq (Rochleder, Z 1868, 711) is probably identical with phloretic acid

o Oxy β phenyl propionic acid C_cH₄(OH) CH₂ CH₃ CO₃H Melilo Melilotic acid drocoumaric acid [83°] S 5 at 18°, 109 at Occurs, partly combined with coumarin, in yellow melilot (Melilotus officinalis) (Zwenger a Bodenbender, A 126, 257, Suppl 5, 100)
Formed by reducing coumarin with sodiumamalgam (Zwenger, A Suppl 8, 32, Dyson, C J 51, 70, Hochstetter, A 226, 355, Tiemann, B 10, 286) Trimetric crystals Its ammoniacal solution turns blue in air Yields salicylic acid when fused with potash Conc HBrAq converts it into the anhydride

Salts - KA'xaq - BaA' 3aq - CaA'2 -Cah', 2aq — Mgh', 4aq — Cuh, aq — Pbh', —
Znh' aq — Agh' bulky pp

Ethyl ether Eth' [34°] Prisms

Methyl derivative

C_sH₄(OMe) CH₂ CH₂ CO₂H [92°] Crystals (from alcohol) (Perkin, C J 39, 416)

Ethyl derivative $C_0H_4(OEt)$ $CH_2CH_2CO_2H$ [80°] Needles (from dilute alcohol) Yields the salts $Ba(C_{11}H_{13}O_3)_2$ and CaA 22aq (Fittig a Ebert, A 216, 153)

Anhydride C.H.O. Hydrocoumann [250] (272°) Got by distilling the acid Tables, sl sol hot water Its oxim C₆H₄<C₀H₄>C(NOH)

18 oily (Tiemann, B 19, 1664) $Amide C_9H_{11}NO_2$ [70°] Needles

m Oxy-β phenyl propionic acid $C_6H_4(OH) CH_2 CH_2 CO_2H$ [111°] Formed by reduction of m-coumaric acid (Tiemann a Ludwig, B 15, 2050) Long needles, insol ligroin Methyl derivative [c 51°] Needles

Oxy-8 phenyl propionic soid [41]C₂H₄(OH) CH₂CH₂ CO₂H Hydropara coumaric acid [129°] Occurs in very slight quantity in human urine (Baumann, H 4, 307) Formed by reducing paracoumaric acid with sodium amalgam (Hlasiwetz a Malin, A 142, 358) Formed also from p nitro-cinnamic ether by reduction followed by the diazo reaction (Stöhr, A 225, 57, cf. Buchanan a Glaser, Z [2] 5, 193) Occurs in putrid meat (Salkowski, B 13, 190). Formed also by putrefactive ferp-0xy-e-pheayl-prepiente acid

C.H.(OH) CHMe CO.H Phloretic acid. [129°]. mentation of tyrosine (Baumann, B 12, 1450;

18, 279) Monoclinic prisms (from ether), sl sol cold water. Gives a bluish grey colour with FeCl. Yields poxy benzoic and when fused with potash—BaA'₂—ZnA'₂2aq S 77 in the cold—CuA'₂2aq—AgA' minute needles

Ethyl ether EtA' Liquid smelling like

rhubarb

Methyl derivative C_eH₄(OMe) CH₂CH₂CO₂H naringenic acid [102°] Hydro - methyl -Feathery crystals or long white needles -A'Ag small needles, sl

Bol hot water — A'2Ba 2aq

Dr methyl ether of the methyl derivative C.H. (OMe) CH. CH. CO.Me [38°], (265°-270°) Formed by methylation of p hydro cou-

maric acid (Eigl, B 20, 2531)

Amide C.H. (OH) CH2 CH2 CONH2 Needles α Oxy $\beta\beta$ di phenyl propionic acid

CHPh₂CH(OH) CO₂H [159°] Formed by saponifying its ether with alcoholic potash Thin needles, v sol alcohol Forms a com Formed by pound [c 53°] when heated with dilute H,SO, at 180°

Ethyl ether EtA' [66°] Got from diphenyl acetic aldehyde cyanhydrin by conver by alcoholic hydrochloric acid into CHPh, CH(OH) C(OEt)(NH2Cl) [135°] and de composition of this body by water (Weise, A. 248, 43) Small plates, insol water

Acetyl derivative [53°] [4 3 1] Di-oxy-phenyl-propionic acid

C, H, (OH), CH, CH, CO, H Hydrocaffer acid Formed by reducing caffeic acid with water and sodium amalgam (Hlasiwetz, A 142, 353) Tri-Its salts are metric crystals, v sol water gummy

Methyl derivative [4 3 1] C₀H₃(OH)(OMe)CO₂H [90°] Formed by reducing ferulic acid with sodium amalgam (Fremann a Nagar, B 11, 650, 14, 965) Minute

tables, v sol alcohol

Methyl derivative [4 3 1] C_oH_s(OMe)(OH)CO₂H [147°] Formed by reduction of isoferulic acid (T a N) Needles

Di methyl derivative C₆H₄(OMe)_rCH₂CH₂CO₂H [[97°] Formed by reduction of C.H. (OMe), CH CH CO, H (T a N) Slender needles (containing aq)

Methylene derivative

 $CH_2 < 0 > C_6H_3 C_2H_4 CO_2H$ Pipero propionic [85°] by reduction Formed CH₂O₂C₆H, CH CH CO₂H (Lorenz, B 13, 758) and by oxidising (B) hydropiperic acid with $Na_{2}CO_{3}$ and $KMnO_{4}$ (Regol, B 20, 421) Needles (from ligroin), sl sol cold water -CaA', aq -AgA' feathery crystals

(4,2,1) D1 oxy-phenyl-propionic acid C.H. (OH) CH2 CH2 CO2H Formed by reducing umbelliferone with sodium amalgam (Hlasiwetz a. Grabowski, A 139, 102) Crystalline, decomposing at 110° Yields resorcin when fused with

potash

Di methyl derivative [105°] Formed C₆H₃(OMe)₂ CH₂ CH₂ CO₄H by reduction of the di-methyl derivatives of (a)and (8) umbellic acid (Will, B 16, 2116) White erystals (from alcohol)

oa-Di-oxy-phenyl-propionic acid O.H. (OH) CH. CH(OH) CO.H. Salicyllactic acid Formed by reduction of o oxy-phenyl-glycidic

acid with sodium amalgam (Plöchl, B 19, 1188) Syrup — ZnA'₂ — CuA'₂ 6aq prisms, v. sol Aq pa Di-oxy-phenyl-propionic soid C₈H₄(OH) OH₂OH(OH) CO₂H [144°] Made

from the corresponding di amido acid by the diazo reaction (Erlenmeyer a Lipp, A 219, 226) Hemispherical groups of needles (containing aq) (from water at 0°), m sol alcohol. Melts at 140° after fusion - CaA', 3aq CaA'₂ 6aq small crystals
D1 oxy phenyl propionic acid

[4 1] C.H. (OH) CH(OH) CH2 CO2H (?) Occurs in urine of dogs fed with much tyrosine (Blendermann, H 6, 256) Needles (containing aq), m sol cold water

aβ-Di oxy phenyl propionic acid

CHPh(OH) CH(OH) CO H B-Phenyl glyceric acid [144°] Formed by the action of alkalis 98, Lipp, B 16, 1287), and by oxidising cumanic acid with dilute KMnO₄ (Fittig, B 21, 920) Monoclinic plates (from ether) At 160° it yields phenyl acetic aldehyde Gaseous HCl yields CoH, CHCl CH(OH) CO2H (Erlenmeyer, jun, B 20, 2466) —AgA' amorphous pp

Di benzoyl derivative [187° Di benzoyl derivative of the methyl

ether [114°] Formed by the action of AgOBz on CHPhBr CHBr CO.Me (Anschutza Kinnicutt, B 12, 538) Small monoclinic crystals

Di benzoyl derivative of the cthylether CHPh(OBz) CH(OBz) CO₂Et [109°]

Isomeride v Atroglyceric acid

Di-oxy-di-phenyl-propionic acid CisHi,O, aq te CH, C(C,H,OH), CO,H Made from phenol, pyruvic acid, and H,SO, at 0° (Böttinger, B 16, 2071) Amorphous mass, carbonising above 268°, v sol acetone Yields an amorphous di acetyl derivative

Tri oxy phenyl propionic acid derivative C_sH₂(OEt), C₂H₄ CO.H [77°] Formed by reduction of the tri ethyl derivative of (a) or (B) asculetic acid with sodium amal gam (Will, B 16, 2111)

An isomeric acid [85°] is got by reducing the di ethyl derivative of daphnetic acid (Will a Jung, B 17, 1087)

Hexa-oxy-di phenyl-propionic acid C,5H,4Oa te CH₃ C(C_eH₂(OH)₃)₂ CO₂H [162°] Formed, together with amorphous C15H12O7, from pyro gallol, pyruvic acid, and H,SO, at 0° (Bottinger, Yields, when B 16, 2404) Resinous mass heated with Ac₂O, the compounds C₁₅H₁₀Ac₂O, [110°] and C₁₅H₈Ac₄O, [c 200°]

References - BROMO , CHLORO , CHLORO NITRO-,

and Iodo-, OXY PROPIONIC ACIDS

p-OXY-DI-PHENYL PROPYLAMINE thyl derivative C₁₅H₁₆NO 16 C₆H₄(OMe) CH₂ CHPh CH₂NH₂ F Formed from

the methyl derivative of a phenyl p coumario nitrile by reduction with alcohol and sodium (Freund a Remse, B 23, 2864) Yellow liquid, slightly volatile with steam —B'₂H₂PtCl₆ [195°]

Aurochloride [87°] Golden plates

OXY-DI PHENYL-PROPYLENE-DIAMINE C₁₅H₁₆N₂O i.e CH(OH)(CH_rNHPh)₂ Made by the action of aniline on epichlorhydrin Needles (from (Fauconnier, C R 107, 250) - B'H,C,O, 1 aq alcohol) [150°] B'H.PtCl, 4aq vellow plates.

Acetyl derivative C₁₅H₁₇AcN₂O aq [100°] Prisms

Netrosamene C.H. (NO) N.O [109°]. DI-p-OXY-DI-PHENYL PROPYLENE Demethyl derivative CH, CH C(C,H,OMe)2. Formed from anisole, AlCl,, and propionyl chloride (Gattermann, B 22, 1130) Plates Yields CO(C,H,OMe), on oxidation The homo-logous CH, CH C(C,H,OEt), crystallises in needles [77°

OXY-PHENYL ISOPROPYL KETONE derivative CoH4(OEt) CO CHMe2 Ethyl[41°] Made from isobutyryl chloride, C.H.OEt, and AlCl, (Gattermann, B 23, 1206) Tables (from ether) Yields an oxim [111°] crystallising in needles

Oxy phenyl propyl ketone C₂H, CO C₆H₄OH [91°] (c 280°) Formed from phenol and butyryl chloride (Perkin, C J 55, 546) Pearly plates

DI - OXY - PHENYL - ISOPROPYL - PYRIM IDINE CH < CPh - N > CMe (OH)

Formed from oxy isobutyramidine hydrochloride, benzoyl acetic ether, and NaOHAq (Pinner, B. 22, 2626) Prisms (from alcohol or benzene)
OXY - TRI - PHENYL - PROPYL - PYRROLE

 $C_{23}H_{23}NO$ a.s $NPr {\stackrel{\rm CO}{<}}{\stackrel{\rm CPh}{C}}{\stackrel{\rm CPh}{C}}{\stackrel{\rm CPh}{C}}$ [105°] Formed from C.H.CBz CHBz and alcoholic propylamine at 100° (Japp a Klingemann, C J 57, 706) Monoclinic prisms [95°-98°] or trimetric prisms $[105^{\circ}]$, abc = 6941 765

DI-0-OXY-DI PHENYL PROPYL ψ-THIO UREA Dimethyl derivative C(SPr)(NH C_sH₄ OMe) N C_sH₄ OMe [58°] Made from di-anisyl thio urea and propyl chloride (Foerster, B 21, 1864) Plates, insol water

OXY-DI PHENYL PYRAZINE hydride NPh CH₂CH₂NPh [148°] Formed from di phenyl ethylene diamine, chloro acetic acid, and NaOAc at 170° (Bischoff a Nastvogel, B 22, 1783, 23, 2026) Crystalline Insol Aq Di-oxy di phenyl pyrazıne

DihydrideNPh CO CO NPh Di phenyl aß diacipi perazine [258°] Got by oxidising the above with CrO, and HOAc, and also by heating di phenyl ethylene diamine with oxalic acid at 200° (B a N) Plates, v sl sol alcohol and ether Nitrous acid forms C₁₀H₁₀N₀O₀ [290°]

Di-oxy di phenyl-pyrazine Dihydride NPh CO CH ON NPh Diphenyl ay diacipi nerazine Di oxy-di phenyl piazine dihydride Made from aniline and chloro acetic and (Hausdorfer, B 22, 1797, cf Meyer, B 10, 1967, Abenius, J pr [2] 40, 491) Needles Alcoholic potash forms phenyl amido acetic acid [127°] on boiling, and in the cold produces NHPh CH₂CO NPh CH₂CO₂H [130°]

Dihydride D1-oxy-phenyl-pyrazine NPh CH, CO NH [158°] Made from aniline and chloro-acetic amide (B) Prisms

Di-oxy-di-phenyl-pyrazine Dihydride NPh CH, CO NPh Diphenyl-as diacipiperasine [152°] Formed by heating the monoanilide of phenyl-imido diacetic acid with Ac₂O

at 160° (Bischoff, B 23, 1990) Needles Nitrous acid yields C16H12N2O2 [c 95°] crystallising in golden plates

 \mathbf{D}_{1} -p-oxy-d₁-phenyl-pyrazine Di-methyl

 $\begin{array}{l} \textit{derivative of the hexahydride} \\ \textbf{C_{e}H_{4}(OMe)N} < \stackrel{\textbf{C}H_{2}}{\text{C}H_{2}} \stackrel{\textbf{C}H_{2}}{\text{C}H_{2}} > N \text{ C_{e}H_{4}OMe} \end{array}$ [233°].

Formed from p anisidine, ethylene-bromide, and NaOAc (Bischoff, B 22, 1782) Tables

Diethyl derivative of the hydride [223°] Gives a nitroso derivative [c 80°]

Tri oxy di phenyl-pyrazine Di ethyl derivative of the tetrahydride

C_eH₄(OEt) N CH₂ CH₂ N C_eH₄ OEt (162°]. Formed from C2H4(NH C6H4OEt), by heating

with chloro acetic acid and fused NaOAc at 150° (Bischoff, B 23, 2030) Crystals, sl sol ether Dr ethyl

Tetra oxy di phenyl-pyrazine derivative of the dihydride C_aH₄(OEt) N CO CH₂N C_aH₄OEt

Formed by heating p ethoxy phenyl amido-acetic acid at 260° (B a N) Needles

OXY PHENYL PYRAZÓLE C₂H₇(OH)N₂. [153°] Got from bromo oxy phenyl pyrazole by reduction with sodium amalgam (Fischer a Knoevenagel, A 239, 201) Needles Sol conc HClAq and alkalis The Na salt forms needles

Oxy-phenyl pyrazole tetrahydride CoH12N O ** NPh CH₂ CH(OH) ? [104°] Formed by the action of phenyl hydrazine on epich'orhydrin in ethereal solution at 15° (Gerhard, B 24, 352) Pearly prisms (from ether), v sol warm water Yields aniline and phenyl pyrazole on boiling with phenyl hydrazine hydrochloride in benzene solution Forms an acetyl derivative -Salt

B'2H2PtCl8 2aq [156°] Yellowish red prisms Oxy-dı-phenyl-pyrazole NPh $<_{
m CPh}^{
m NH}$ CO phenylpyrazolone [251°] Formed by heating cinnamoyl phenyl hydrazine (Knorr, B

1108) Needles (from alcohol), exhibiting green fluorescence

Oxy di phenyl pyrazole NPh $<_{
m CO}^{
m N}$ CPh $_{
m CO}$ CH $_{
m 2}$

[137°] Formed from benzoyl acetic ether and phenyl hydrazine (Knorr a Klotz, B 20, 2546) Yields, with nitrous acid, the red compound NPh CPh [200°] Diazobenzene chlor ide forms C_xHPh₂N₂O(N₂Ph) [171°] hydrazıne converts it into di oxy tetra phenyl dıpyrazyl melting above 300° — B'HCl — B'H,SO, Powder Decomposes at 237°

Oxy di phenyl-pyrazole NPh

[196°] Formed from a phenyl glyoxylic acid and phenyl hydrazine (Wislicenus, B 20, 2932) Plates (from EtOH), sol alkalis, sl sol ether

D1-oxy-phenyl metapyrazole probably C.H. CH N C₂H₈N₂O₂ [182°]

C(OH) N/ tained by boiling phenyl uramido aceto nitrile C_eH_a CH(CN) NH CO NH₂ (from benzaldehydecyanhydrin and urea) with dilute HCl Colourless dimetric plates Dissolves readily in alkalis (Pinner a Lifschutz, B 20, 2355) OXY PHENYL PYRAZOLE CARBOXYLIC

ACID C₁₀H₈N₂O₃ te NPh CO OH₂ [268°] Formed by the action of HCl or NaOH on the

phenyl hydrazide of oxalacetic ether (Buchner B 22, 2931) Colourless needles, v sl sol cold FeČl₃ colours its solution dark blue

• Ethyl ether [182°] Formed by heating the above phenyl hydrazide by teelf (Wislicenus, **A** 246, 306)

OXYPHENYL PYRIDINE O11 H, NO Formed by heating aniline chelidonate (Lerch, M 5, 407) Crystallises from water in needles (containing aq)

Oxy-di-phenyl-pyridine C, H, NO NH CPh CH CO [267°] Formed by heat ing dehydro benzoyl acetic acid with alcoholic NH, at 160° (Feist, B 23, 3736) Plates

DI OXY-PHENYL PYRIDINE CARBOXYLIC ACID C,H(OH)2NPh CO2H Made by boiling a solution of comenic acid with aniline (Mennel, J pr [2] 32, 177) Tetrahedra (containing aq), m sol water Coloured violet by FeCl.

OXY PHENYL PYRIMIDINE C,0H,N,O 2 e CPh N C(OH) CH [199°] Made by heating its carboxylic acid (Pinner, B 22, 2616) Small prisms, sl sol hot Aq, v sol alkalis and acids

Oxy di phenyl pyrimidine $C_{16}H_{12}N_2O$ CPh < N - CPh > CH[284°] Formed from benzamidine hýdiochloride, benzoyl acetic ether, alcohol, and dilute (10 pc) NaOH (Pinner, B 22, 1626) Formed also by heating amido diphenyl pyrimidine with HClAq at 180° (Schwarze, J pr [2] 42, 15) Needles, v sl sol hot alcohol

Oxy tri phenyl pyrimidine C₂₂H₁₆N₂O [340°] Formed by heating the corresponding amido compound with HClAq at 170° (Wache, J pr [2] 39, 255) Needles

Dı oxy di phenyl pyrımıdıne Ethyl derivative C,H,(OEt) C&N CPh C(OH) CH [274°] Formed from p ethoxy benzamidine and benzoylacetic ether (Pinner, B 23, 2955)

OXY PHENYL PYRIMIDINE CARBOXYLIC ACID CPh N C(CO₂H) CH [247°] Formed from benzamidine hydrochloride, oxalacetic ether, and dilute (10 pc) NaOH (Pinner, B 22, 1628, 2616) Granules, sl sol water -BaA" CaA', Prisms — Amide prisms, sl sol water — Benzamidide C₁₈H₁₄N₄O₂ [263°]

Oxy di phenyl-pyrimidine carboxylic acid $CPh \leqslant_{N C(OH)}^{N CPh} \geqslant_{C CO, H}$ [236°] Made by oxidising oxy di phenyl methyl pyrimidine with KMnO₄ (E von Meyer, J pr [2] 40, 303) Yellowish prisms (from alcohol, Yields oxydi phenyl pyrimidine [284°] on heating

Di oxy phenyl pyrimidine carboxylic acid Ethyl derivative

 $C_rH_4(OE4)$ $C < N = C(OC_2H)$ OH [246°] Made from p-ethoxy benzamidine and oxalacetic ether (Pinner, B 23, 2956) Needles, si sol hot alcohol —Salt C.H. (OEt) CN2H4A. [280°]. Vor. III.

OXY-TRI PHENYL-PYRROLE C., H, NO 2.4. NH CO CPh CH Mol w 311 [221°] Formed by boiling C.H. CBz CHBz for a long time with alcoholic ammonia (Japp a Klingemann, B 22, 2884, C J 57, 682) Triclinic crystals, a b c = 779 1 512, $\alpha = 78^{\circ} 56'$, $\beta = 73^{\circ} 23'$, $\gamma = 87^{\circ} 32'$ (Tutton, C J 57, 720) Sl sol hot alcohol

Dihydride NH CHPh CH₂ [201°] Formed by reduction with sodium and amyl Ac₂O at 180° yields an acetyl deriva alcohol tive NAc CHPh CH₂ [105°].

o Oxy-tri-phenyl-pyrrole

C₆H₄(OH) N CPh CH [176°] Made by heating its carboxylic acid with lime (Paal a Braikoff, B 22, 3094) Yellowish needles, v sol alkalis

Oxy-tetra phenyl-pyrrole

C₂₈H₁NO 1 e NH CO CPh, [207°]. Formed by heating CPhBz CPhBz with alcoholic NHa at 200° (Klingemann a Laycock, C J 59, 144, B 24, 513) Pale yellow plates

Dihydride NH CHPh CHPh [2379]

Oxy tetra phenyl pyrrole C₂₈H₂₁NO Formed from CPhBz CHBz and alcoholic NH, at Yellow prisms Changed into the iso meride [207°] by heating to 310°

o-OXY TRI PHENYL-PYRROLE CARBOXY-LIC ACID $C_eH_4(OH) N < {CPh CCO_2H \over CPh CH}$ [245°]

Made from its ethyl ether [159°] which is got by the action of o amido phenol on phenacyl benzoyl acetic ether (Paal a Braikoff, B 22, 3093) Nodular groups of needles, v sol ether

OXY-PHENYL-QUINAZOLINE

Dihydride C.H. CH2 NPh CO [143°] Formed from phenyl-ω oxy tolyl urea and HCl (Söderbaum a Widman, B 22, 1670) Needles

Oxy phenyl quinazoline

C,H,COH) N CPh [234°] S (alcohol) 2. Formed by heating benzoyl o amido benzamide (Korner, J pr [2] 36, 157) Needles, insol water —B'₂H₂PtCl₆ brick red needles

 $C_6H_4{<}^{CO\ NPh}_{N=CH}$ Oxy phenyl quinazoline [189°] Formed by oxidation of phenyl quinazoline dihydride with KMnO, (Paal a Busch, B 22, 2691) Plates, v sol benzene With hydrazine N₂H₄ it forms C₆H₄ C(N₂H₂) NPh CH [214°] -Platinochloride [204°] — B'HCl [above 300°] Yellow needles

Di-oxy phenyl quinazoline CH₂ CH₂ C N — CPh CO CH₂ C C(OH) N [272°] Dihydride [272°] Formed from di oxy terephthalic ether, dihydride, and benzamidine (Pinner, B 22, 2623) Slender needles. sol alkalis, sl sol alcohol

OXY PHENYL-QUINAZOLINE CARBOXY-LIC ACID C'H' CON C'H' CO'H [820°]. Made by oxidising oxy p tolyl-quinazoline (Paal Busch, B 22, 2683) White crystals Busch, B 22, 2683) 8 0

(a) - OXY - (Py 1) - PHENYL - QUINOLINE C,H,NO . C,H, C(C,H,OH) CH Phenolquantum [243°] Formed by diazotising (a)-amido (Py 1)-phenyl-quinoline [150°], and boiling the dilute H₂SO₄ solution (Kænigs a Nef, B Colourless flat needles or plates Volatilises undecomposed V sol alcohol and chloroform, sl sol benzene, nearly insol ether By CrO, and H.SO, it is oxidised to cinchonic acid. The hydrochloride forms glistening plates, the sulphate yellow tables, both are v sol hot water, sl sol cold The platino chloride forms hair-fine yellow needles, v sol conc HCl The K and Na salts are colourless glistening plates, which dissolve in water with a yellow colour

(β) 0xy (Py 1) phenyl quinoline C₁₅H₁₁NO ε ε C_εH₄ N C(C₁C₂H₄OH) CH Phenol quinoline

[235°] Formed by diazotising the corresponding amido compound [198°] and boiling the dilute H₂SO₄ solution (Kœnigs a Nef, B 20, 630) Colourless granular crystal Sl sol alcohol, nearly insol ether Volatilises undecom posed Dissolves with a yellow colour in alkalis and acids By CrO, and H,2SO, it is oxidised to cinchonic acid KOH fusion yields di oxyphenyl - quinoline [305°] The sulphate crystallises in glistening yellow needles, the hydrochloride in yellow tables, both are m sol cold water

o Oxy (Py 3) phenyl quinoline

 $\mathrm{C}^{e}H^{4} \stackrel{\mathrm{CH}}{<_{\mathrm{CH}}} \stackrel{\mathrm{CH}}{<_{\mathrm{CH}}}$ [115°] Got by heating its (Py 1)-carboxylic acid [238°] (Doebner, A 249, 101) Light yellow needles (from alcohol), sol alkalis and acids -B'2H2PtCl, -B'C,H3N2O, [184°] Yellow needles

m 0xy-(Py 3) phenyl-quinoline C_eH₄ CH CH N C C_eH₄OH [156°] Fo [156°] Formed by the action of nitrous acid upon m amido phenylquinoline (Miller & Kinkelin, B 18, 1908) Long needles, v sol alcohol and ether

p Oxy (Py 3) phenyl quinoline $\mathbf{C}_{e}\mathbf{H}_{i} < \mathbf{N} \mathbf{C}\mathbf{C}_{e}\mathbf{H}_{4}\mathbf{O}\mathbf{H}$ [238°] Formed from the amido-compounds (Weidel, M 8, 127) Monoclinic needles, insol water, v sol hot benzene Yields quinoline carboxylic acid [157°] on oxidation Yields a crystalline tetra hydride on reduction —B'HCl 2aq —B'₂H₂PtCl₆
Acetyl derivative [123°] Plates

Acetyl derivative [123°]

(Py 1, 4) Oxy-phenyl quinoline C_oH₄ COH CH [254°] Former [254°] Formed, by heating to 250°, from the phenyl β amido cinnamic ether NPhH CPh CH CO2Et, got by the action of aniline on benzoyl acetic ether (Conrad a Limpach, B 21, 521, Knorr, A 245, 877) Got also by heat ing its carboxylic acid (Just, B 19, 1462) Plates, v sl sol water, insol ether -B'HCl [230°]. Needles (from alcohol) $-B'HCl\frac{1}{2}aq(J)$

(B 2) Oxy-(Py 3) phenyl-quinoline Me-thyl derivative CH CH — C N CPh [183°] Got by heating its carboxylic acid [237°] (Doeb ner, A 249, 106) Plates (from dilute alcohol) B'HOl needles, sol. hot water -B',H,PtCl,

Picrate [205°].

(B 4)-Oxy (Py 8)-phenyl quinoline. ÇH CH —— Ç CH ÇH derivative ČH C(OMe) Č N ČPh Formed by heating its carboxylic acid [216°]
(D) Oil—B'₂H₂PtCl₄ 2aq orange needles
Di oxy phenyl-quinoline C₁₅H₁₁NO₂ 10 •

 $C_0H_4 < N = COH (?)$ [305°] by potash fusion from (β) oxy (Py 1) phenyl quinoline [235°], the yield being 75 p c (Koenigs a Nef, B 20, 632) Needles, v sol alcohol Has no basic properties An isomeride, solid at 315°, appears to be formed from (a)-oxy (Py 1)phenyl quinoline by potash fusion.

[114°] Di oxy-phenyl quinoline in small quantity when p amido (Py 3) phenyl quinoline is acted upon by nitrous acid (Weidel, M 8, 127) Prisms, insol water Reduced by

zinc dust to (Py 3) phenyl quinoline
Di-oxy phenyl-quinoline
C(OH) CH C CH CH

[247] [247°] Formed $CH = CHC - N C(C_6H_1OH)$ from (B 2) oxy p amido (Py 3) phenyl quinoline by the diazo reaction (Weidel a Georgievitch, M 9,138) Pale-yellow mass of hair like needles, sl sol hot water Yields (Py 3) phenyl quinol ine when distilled with zinc dust

Di-oxy-(Py 1) phenyl-quinoline Ç(OH) CH C C(C,H, OH) ÇH derivative CH CH—C N——CH Got by boiling the diazo compound of m amido (Py 1)-phenyl (B 2) methoxy quinoline with dilute H₂SO₄ (Miller a Kinkelin, B 20, 1922) Plates Its solution in dilute H₂SO₄ gives with chlorine water, a little NaOH, and ammonia, a dark green colour

Tetrahydride [111°] Tablets Gives a deep green with FeCl, and HCl—B'HCl plates Tetrahydride [111°] (Py 4)-OXY (Py 2) PHENYL-ISOQUINOL-

CH CPh C(OH) N Isobenzylidene

phthalimidine [197°] Formed by the action of ammonia on deoxybenzoin o carboxylic acid CH2Bz C6H4 CO2H Prepared by heating crude isobenzylidene phthalide (15 g) with alcoholic NH_3 (30 c c) at 100° for 8-10 hours (Gabriel, B 18, 2449, 3470, 19, 830) Triclinic crystals, abc = 8608 1?, $\alpha = 88^{\circ}$ 28', $\beta = 111^{\circ}$ 24', $\gamma = 74^{\circ}$ 47' Sl sol cold alcohol By heating with POCl, or PCl, it is converted into (Py 4)chloro (Py 2) phenyl isoquinoline, PCl, yields (Py 1,4) di chloro (Py 2) phenyl quinoline Nitrous acid converts it into (Py 1) nitro-(Py 4) oxy (Py 2) phenyl isoquinoline

Ethylether C₁₈H₁₀N(OEt) [46°] Formed by heating chloro phenyl isoquinoline with alcoholic sodium ethylate (Gabriel, B 19, 835) Flat colourless needles, v sol ordinary solvents. weak base -B'2H2Cl2PtCl4 reddish pp.

Di oxy-phenyl-iso-quinoline

C,H, COMNH [257°] Formed from nitro benzylidene phthalide, P, and HI (Gabriel, B.

18, 3471, 20, 2866) Crystals, sl sol boiling Aq Methyl ethers Two isomeric methyl ethers [237°] and [121°] may be prepared Both are crystalline.

Reference — CHLORO ONY PHENYL ISOQUINOL-

(Py 1, 8, 2)-OXY PHENYL-QUINOLINE CARBOXYLIC 'ACID $C_{\bullet}H_{\bullet} < \stackrel{C(OH)}{\sim} \stackrel{CCO_2H}{\sim} CPh$

Made from its ethyl ether [262°] which is formed by heating NPh CPh CH(CO2Et)2 to 150°, alcohol being split off (Just, B 18, 2632, 19, 1462) Crystals (containing aq), v sl sol hot water —AgA' sl sol water

o Oxy (Py 3, 1)-phenyl quinoline carboxylic

acid C₆H₄ C(CO₂H) CH C C₆H₄ OH [238°] Made from salicylic aldehyde, aniline, and pyruvic acid (Doebner, A 249, 98) Needles, v sol alcohol—AgA'—H₂A'₂H₂PtCl₆ golden yellow needles.

(B 2, Py 3, 1) 0xy phenyl quinoline carb-lic acid Methyl derivative oxylic acid C(OMe) CH C C(CO₂H) CH

Phenyl quinic --C--N CPh $[237^{\circ}]$ Formed by heating together acidequimolecular quantities of pamido anisole, benzoic aldehyde, and pyruvic acid in an alco holic solution (Doebner, A 249, 105) Needles, insol water -AgA' -H2A'2H2PtCla orange red crystals

(B 4, Py 3, 1) Oxy phenyl quinoline carboxylic acid Methyl derivative
CH CH — C C(CO₂H) CH CH C(OMe) C — N CPh [216°] Formed in like manner from [2 1]C,H4(NH2) OMe, benzoic aldehyde, and pyruvic acid (D) needles —PbA', aq —AgA' —H₂A'₂H₂PtCl

DI OXY DI-PHENYL QUINOXALINE

ethyl derivative CH C(OEt) C N CPh CH C(OEt) C N CPh [163°] Formed by the action of benzil and NaOAc on an alcoholic solution of the di ethyl ether of (a) di amido hydroquinone (Nietzki & Rechberg, B 23, 1212) Yellow needles

Di oxy di phenyl quinoxaline Dihydride

Di methyl derivative

C.H. N CH C.H.OMe Phenylanisaldehydine Formed from anisic aldehyde and

phenylene o diamine (Rugheimer a Ladenburg, B 11, 1660) Needles (from alcohol)

g-OXY PHENYL-SUCCINIC ACID

 $\mathbf{C_6H_5}$ $\mathbf{C}(\mathbf{OH})$ $\mathbf{CO_2H}$ $\mathbf{CH_2}$ $\mathbf{CO_2H}$ Phenyl malic acid [188^] S 159 at 15° Formed by heat ing a bromo phenyl succinic acid with hot water (Alexander, A 258, 76) Needles (from chloro-Yields, on heating, phenyl maleic anhydride [119°], phenyl fumaric acid [161°], and a sublimate [106°] probably atropic acid

β Oxy-phonyl succinic acid C.H., CH(CO.H) CH(OH) CO.H [150°-160°]. S 37 35 at 15° Got from C.H., CH(CHO) CO.Et, potassium cyanide, and HCl (A) Crystalline powder, v sol water Yields phenyl maleic an-

hydride when heated to 160°

D1-0xy-di-phenyl succinic acid CO.H CPh(OH) CPh(OH) CO.H The mtrile of this acid CPh(OH)Cy CPh(OH)Cy [132°] is formed by union of benzil with HCy (Zinin, A 34, 189, Jacoby, B 19, 1519) It is converted It is converted in the cold by HOAc saturated with HBr into the amide C1. H1. N2O4 [150°-230°] (Burton, B 16,

aniline' by the diazo reaction (Krafft, B 1165, 22, 821), and also by the action of SCl. on phenol in presence of CS₂ (Tassinari, G 17,

Silvery plates, sl sol cold water.

Dr acetyl derivative [93°]

An isomeride [129°] may be obtained from S(C,H,Br OH), [176°] by reduction with zincdùst (Ť)

Reference -DI BROMO DI-OXY-DI PHENYL BUL-PHIDE

Di p-oxy-di-phenyl disulphide

 $S_2(C_0H_4OH)_2$. [151°] Formed by oxidising poxy phenyl mercaptan (thic hydroquinone) with dilute FeCl, (Leuckart, J pr [2] 41, Yellow needles, v e sol alcohol

Diacetyl derivative [89°]. Plates Di o oxy di-phenyl disulphide

S₂(C₆H₄OH)₂ Formed by heating sodium phenate (2 mols) with sulphur (1 at) at 190° (Haitinger, M 4, 165) Thick oil Yields o oxy-phenyl mercaptan on reduction — NaHA" 6aq — KHA" 5aq — PbA" yellow pp

Di methyl derivative Me₂A" [119° cor].

Yields anisole o sulphonic acid on oxidation

DI-OXY DI-PHENYL SULPHONE SO₂(C₆H₄OH)₂ [239°] SG 151 366 Formed by heat ng phenol (2 pts) with fuming H SO₄ (1 pt) at 190° (Glutz, A 147, 52, Annaheim, J pr [2] 1, 14, 2, 385, B 8, 1059, 11, 1668, A 172, 28) Trimetric crystals, a b c = 1 283 1 0 534. V sol hot water and alcohol—K,A" Sol. alcohol (Guareschi, G 8, 246)—NH,HA"—NaHA"aq—AgHA"—Ag,A"

Di methyl ether Me₂A" [130°] Di ethyl ether Me₂A" [130°] Diethylether [159°] Laminæ Di isoamyl ether [98°] Plates

Di oxy di-phenyl sulphone SO2(C6H4OH)2 [187°] Got from its acetyl derivative which is made by oxidation of CoH4(OAc)(SH) [1.2 or 3] (Tassinari, C C 1888, 1354) Crystalline, al.

References -DI BROMO, DI BROMO DI NITRO-, DI CHLORO, TETRA IODO, DI IODO-DI-NITRO, and DI NITRO, DI OXY DI PHENYL SULPHONE

OXY PHENYL SULPHONIC ACID v PHENOL

SULPHONIC ACID

Oxy diphenyl sulphonic acid C₁₂H_s(OH) SO₂H Made, together with the disulphonic acid, by heating oxydiphenyl (1 pt) with H₂SO₄ (3 pts) (Latschinoff, JR 5, 54) —
KA' aq plates, sl sol water—BaA', aq—
CaA', 3aq—K₂CuA', 6aq green laminæ
Oxy diphenyl disulphonic acid

C₁₂H₂(OH)(SO,H)₂ Made as above — D₁ oxy diphenyl disulphonic acid -K,A" 1 daq.

 $[4\ 2\ 1]\ C_sH_s(OH)(SO_sH)\ C_sH_s(SO_sH)(OH)\ [1\ 2\ 4]$ Made from benzidine disulphonic acid by the diazo reaction (Limpricht, A 261, 334) Crystalline mass The K salt forms laminæ, v e sol. water —BaA" 2aq —PbA" 4aq rhombohedra.

Di p-oxy diphenyl disulphonic acid $\mathbf{C}_{12}\mathbf{H}_{6}(\mathbf{OH})_{2}(\mathbf{SO_{3}H})_{2}$ Got by warming di-oxy-diphenyl with fuming H₂SO₄ (Doebner, B 9, 180). Probably identical with the preceding acid. prisms, sl sol cold water

D1-p-oxy-diphenyl trisulphonic acid $C_{12}H_3(\tilde{O}H)_2(SO_3H)_3$ Formed, together with the tetra-sulphonic acid, from benzidine by diazotis-DI-OXY-DI-PHENYL SULPHIDE ing and warming with cone H₂SO₄(Griess, J 1866, S(C₂H₂OH)₂. [151 5°] Formed from 'thio- 462) — Pb₂C₁₂H₂S₂O₁₂ 2aq — Pb₂C₁₂H₄S₂O₁₂ 2bQ.

Di p-oxy-diphenyl tetrasulphonic acid C₁H₄(OH),(SO,H), Made as above —Ba,A'v 5aq prisms —Pb,C,H,S,O₁₂ amorphous pp a-OXY-PHENYL-SULPHONO-ISOBUTYRIO

ACID C.H. SO. CH. CMe(OH) CO.H [121°]
Made by oxidising CH. (SPh) CMe(OH) CO.H [1219] with KMnO, in the cold (Delisle, A 260, 259) Prisms (from ether) —KA 2aq needles —BaA'. OAA', aq groups of needles
OXY-PHENYL SULPHURIC ACID

C.H. (OH) O SO. OH The K salts of the o-, m-, and p-compounds are formed by the action of K₂S₂O, on potassium pyrocatechin, resorcin, and hydroquinone respectively (Baumann, B 11, They are crystalline, sol water, and unstable Potassium pyrogallol yields, in like manner, C₈H₃(OH)₂SO₄K crystallising in needles 8

 $C(OH)^{\nearrow N}$ OXY-PHENYL-THIAZOLE CH CPh Formed from bromo acetophenone by the action of xanthamide (Hubacher, A 259, 249), or by successive treatment with barium sulphocyanide and dilute HCl (Arapides, A 249, 14, cf Dyckerhoff, C J 32, 327) Needles, insol water, sol cold NaOHAq Converted by POl, into chloro-oxy-phenyl thiazole [206°] and another body [98°] (Schatzmann, A 261, 18). Sodium and Etl yield SH CODNET [71°], which on heating with HCl at 220° gives NEtH.

Di-exo-o-oxy-phenyl-thiazole dihydride $^{\mathrm{S-CO}}_{\mathrm{CH_2\,CH_2}}$ N $_{\mathrm{c}}^{\mathrm{H_4OMe}}$ Methyl derivative [116°] Formed by the action of boiling alcoholic chloro acetic acid on the product of the action of OS₂ on the substance formed from ethylene bromide and di anisyl thio-urea (Foerster, B 21, 1867 Plates, v e sol alcohol

p-OXY PHENYL THIOCARBIMIDE Acetyl derivative C.H. (OAc) NOS [36°] Made by heating di p oxy di phenyl urea with Ac.O (Kalckhoff, B 16, 1831) Plates, sol alcohol

Methyl derivative C.H. (OMe) NCS (265°) Formed from anisidine and CS₂ (Hofmann, B 20, 1796, cf Salkowski, B 7, 1012)

Isomeride OXY METHENYL AMIDO PHENYL-MERCAPTAN

D1-oxy phenyl-thiocarbimide Dr-methul derivative O.H. (OMe), NCS Formed by heating $CS(NH C_0H_1(OMe)_2)_2$ with cone HClAq (Bechhold, B 22, 2381) Occurs in three crystalline forms [57°], [120°], and [155°] Sol.

aniline and H.SO.
DI-0-OXY-DI-PHENYL-THIOHYDANTOIN Dr-methyl derivative C17H16N2SO3 ie C.H.(OMe) N C N(C.H.OMe) [190°] S CH, CO

from di-anisyl thio urea and fused chloro acetic acid (Foerster, B 21, 1867) Needles

v-OXY PHENYL-THIO-UREA C,H,N2SO 2 e **C**_e**H**_s**NH CS NH**(**OH**) [108°] Formed from phenyl-thiocarbimide and aqueous hydroxyl amine (Schiff, E Fischer, B 22, 1935, Tiemann, B 22, 1939, Von der Kall, A 263, 260, Voltmer, B 24, 878) White plates, insol water, al sol. ether, v sol alcohol Fehling's solution ppts Cu.S Dilute soids and alkalis decompose it, yielding phenyl cyanamide

Methyl derivative NHPh CS NH OMe [1169] Formed from phenyl-thiocarbimide and

methyl-hydroxylamine.

Ethyl derivative [103°]. Prisms Decomposed, by boiling its alcoholic solution, into phenyl cyanamide, alcohol, and S

Bensyl derivative Prisms [115°]

o-Oxy-phenyl-thio-urea C₆H₄(OH) NH CS NH₂ [161°] Made from oamido phenol hydrochloride and potassium sulphocyanide (Bendix, B 11, 2263) Needles, sol. hot water —B',H,PtCl,
Methyl derivative

O.H. (OMe) NH OS NH₂ [152°] alcohol) (Muhlhauser, B 13, 923) [152°] Needles (from

Ethyl derivative [110°] Tablets, sol alkalıs (Berlinerblau, J pr [2] 80, 406)

p-Oxy phenyl thio-urea [4 1] $C_6H_4(OH)$ NH CS NH₂ [214°] Got by evaporating to dryness on the water-bath, a so lution of potassium sulphocyanide and p amido phenol hydrochloride (Kalckhoff, B 16, 375). Tables, sl sol cold water

Ethyl derivative Crystalline (B)

o Oxy-diphenyl-thio-urea NHPh CS NH C.H.OH [146°] Formed by the action of phenyl thiocarbimide on o-amidophenol (Kalckhoff, B 16, 1829) White pearly plates Heated by itself or with HgO it loses H₂S, yielding anilido carbamido phenol

Methyl derivative NHPh CS NHC,H,OMe NHPh CS NHC₈H₄OMe [127°] Formed from anisyl thiocarbimide and aniline, and also from phenyl-thiocarbimide and anisidine (Foerster, B 21, 1868) Prisms With ethylene bromide it forms crystals [143°] whence platinic chloride yields (C16H16N2OS)2H2PtCl6

 $p extsf{-}0 ext{xy}$ di-phenyl-thio urea NHPh CS NH C₆H₄OH p Oxy throcarbanılıde [162°] Formed by the action of phenyl throcarbimide on p amido phenol (K) V sol alcohol and alkalıs, nearly ınsol water

Acetyl derivative [137°] Insol alkalıs Di o-oxy-di-phenyl thio urea derivative CS(NH C.H.OMe), [135°] Formed from o anisidine, CS₂, and alcoholic potash (Muhlhauser) Formed also from anisidine and thio urea in alcoholic solution (F) Needles, sl sol water With methyl iodide it forms C₀H₄(OMe)N C(SMe) NH C₀H₄OMe [87°] EtI forms C₁H₂₀N₂SO₂ [88°5°], while propyl iodide gives C₁₈H₂₀N₂SO₂ [58°] Ethylene bromide gives CH₂ CH₂N C₆H OMe orystallising in trimetric prisms [186°] and yielding C₁₀H₁₁NS₂OMeI [c 141°] and, on boiling with alcohol and chloroacetic acid, S < C2H, NC4H,OMe [116°]

D1-p-oxy-d1-phenyl th10-urea [22 from p amido phenol and CS_2 (K) [222°] Pearly plates, v sol alkalıs

Di-methyl derivative [185°] (Salkowski, B 7, 1012) Sl sol. alcohol

Di-oxy-di-phenyl-thio urea Dr-methyl derivative NHPh CS NH C.H. (OMe)2 [137°] Formed by the combination of phenyl thiocarbamido-di methyl-hydroquinone with (Baessler, B 17, 2123) Minute needles, v sol. hot benzene and hot alcohol

Tetra-oxy-di phenyl thio urea Tetra. methyl derivative CS(NH CoHs(OMe)2)2 [160°] Formed from the di methyl derivative of amido resorcin and OS₂ (Bechhold, B 22, 2380). White mass (from alcohol-ether), insol alkalis

An isomeride [109°] is formed from the dimethyl derivative of amido - hydroquinone (Baessler)

Reference - DI CHLORO DI OXY-DI PHENYL-

OXY-PHENYL-TOLYLAMINE v Tolyl-AMIDO PHENOL

TRI OXY-DI-PHENYL-TOLYL-CARBINOL Anhydride CoH16O, ie

 $C_6H_4(OH)$ $C_6H_4(OH)$ C_6H_4 RosolicCorallin Formed by the action of nitrous acid on rosaniline (Caro a Wanklyn, J pr 100, 49, A 179, 192) Got also by heating a mixture of phenol and cresol with H₂SO₄ and arsenic acid (Zulkowsky, B 10, 1201) Red plates with green lustre, nearly insol water, sol chloroform, alcohol, and acids Alkalis form a red solution Reduced by sodium amalgam to trioxy diphenyl tolyl methane Water at 240° yields phenol and C.H.(OH) CO C.H.Me(OH) KCy followed by HCl forms crystalline C.H.(NO.)

whence Ac₂O yields C₂₁H₁₄Ac₂NO₂ [142°] p-OXY-PHENYL p-TOLYL-HYDRAZINE

Ethyl derivative C.H. (OEt) NH NH C.H.Me Formed by reducing C₆H₄(OEt) N₂ C₆H₄Me with alcoholic ammonium sulphide (Noelting a Werner, B 23, 3258, Bl[3] 4, 794) Needles, v sol hot alcohol The isomerides C₆H,NH NHC₆H,Me(OEt)[1 3 4] [76°] and C₆H₃NH NHC₆H₃Me(OEt) [1 5 2] [105°] are formed in like manner

DI ONY PHENYL TOLYL KETONE

C₆H₄(OH) CO C₆H₃Me(OH) [200°] Formed by heating rosolic acid with water at 220°-250° (Graebe a Caro, A 179, 196) Crystals, sol hot water

Di acetyl derivative [150°] Needles Di oxy phenyl tolyl ketone Anhydride C.H. CO>C.H.Me [105°] Made by boiling p tolyl salicylate for a long time (Graebe a. Feer, B 19, 2612) V e sol hot alcohol

Tri oxy phenyl-tolyl ketone $C_cH_1(OH)$ CO $C_sH_2Me(OH)_2$ Anhydride $C_{14}H_{16}O_3$ [140°] Made by fusing salicylic acid with orcin and ZnCl₂ (Michael, Am 5, 95) Yellow needles (from alcohol) —NaA' 1½aq

Acetyl derivative C. H.AcO, [152°] DI OXY-PHENYL-DI-TOLYL METHANE

CHPh(C₆H₃Me OH)₂. [171°] Formed from o-oresol benzon and boiling SO₂Aq (Schroeter, A 257, 70) Yellow needles Yields a di bromoderivative [130°] and a di nitro-derivative [127°

Di acetyl derivative C₂₁H₁₈Ac₂O₂ [94°] Di benzoyl derivative [915°] Plates Tri oay-di-phenyl-tolyl methane

C₂H₂Me(OH) CH(C₂H₄OH)₂ Phenolphthalol [190°] Obtained by boiling phenol phthalin CO₂H C₂H₄ CH(C₂H₄OH)₂with HOAc and sodium-amalgam (Baeyer, A 202, 87) Prisms (from dilute HOAc), v sol alcohol

Tri-acetyl derivative C26H24O6 [40°] Tri-oxy di-phenyl-tolyl-methane CsoH18O2 5.6 C.H.Me(OH) CH(C.H.OH). Leucorosolic acid Got by reducing rosolic acid with potash and sinc-dust (Graebe a Caro, A 179,198) Needles (from alcohol), v sl sol water

Tri acetyl derivative. [149°]. Needles.

DI OXY-PHENYL O TOLYL PYRAZINE.

NPh CH C(OH) CH N C, H, Me. Dihudride [166°] Formed by heating aniline with chloroacetyl o tolyl amido acetic acid at 160° (Abenius, J pr [2] 40, 443) Formed also by the action of o toluidine on chloro acetyl phenyl amido-acetic acid in presence of NaOAc (Bischoff, B 23, 1996) White needles, v e sol hot alcohol The isomeric compound from p-toluidine also crystallises in needles [221°

OXY-PHENYL-p-TÖLYL-PYRIMIDINE

C_eH₄Me C N CPh C(OH) CH [above 290°] Made from tolenyl amidine and benzoyl acetic ether (Pinner, B 23, 3826) Slender needles, sl. sol hot alcohol

ω OXY PHENYL o TOLYL-THIO-UREA

CH₂(OH) C₆H₄ NH CS NHPh [c 136°] Made from phenyl thiocarbimide and o amido benzyl alcohol (Söderbaum a Widman, B 22, 1671). Alcohol and HgO convert it into Prisms C₆H₄<0 [146°]

ω OXY-PHENYL TOLYL-UREA

CH2OH C6H4 NH CO NHPh [191°] Made from o amido benzyl alcohol and PhNCO (Söderbaum a Widman, \hat{B} 22, 1670) Needles

v OXY-PHENYL UREA C.H.,NH CO NH OH [140°] Made from phenyl cyanate and aqueous hydroxylamine (E. Fischer, B. 22, 1935, von der Kall, A. 263, 264) Crystals, v. al. sol. water, sol. alkalis. Reduces hot Fehling's solution On boiling with alkalis it yields aniline, CO,, and hydroxylamine Benzyl derivative

NHPh CO NH OCH₂Ph [106°] Needles (Tremann, B 22, 1940, Voltmer, B 24, 384)

o Oxy phenyl-urea C_eH₄(OH) NH ĆO NH₂ Made from o amido phenol hydrochloride and potassium cyanate (Kalckhoff, B 16, 874) Prisms, v sol water

Methyl derivative

C₆H₄(OMe)NH CO NH [147°] Crystals (Muhlhauser, B 13, 922, A 207, 244)
p-0xy phenyl-urea C,H₈N₂O₂ [168°] (K).
Needles or tables, sol acids and alkalis

Ethyl derivative [160°] Made from C.H.(NH2) OEt and KCyO (Berlinerblau, J pr [2] 30, 103) Nitrous acid passed into its alcoholic solution forms brick-red crystals of C,H,,N,O,

Di-o-oxy di-phenyl urea D1-methyl derivative CO(NH C,H, OMe), [182°] Made from COCl, and o anisidine (M, Conrad, B 21, 1649) Crystals, v sol alcohol

Di p oxy-di phenyl urea Dr-methyl de-[234°] Prisms or rivative C15H16N2O2 needles (Lossen, A 175, 295, Pieschel, A 175, 812) V sl sol hot alcohol

8-0XY PHENYL VALERIC ACID C,H,O, v.e CHPh(OH) CMe2 CO2H Phenyl-oxypivalic acid [134°] Formed from benzoic aldehyde, sodium isobutyrate, and isobutyric anhydride by Perkins's reaction (Fitting a Jayne, A 216, 119, Ott, A 227, 61) Needles, sl sol cold water. Split up at 150° into CO, and phenyl-butylene.-BaA', 4aq —CaA', 4aq plates, m. sol. water

Acetyl derivative [187°]. Monochnic orystals (from CS₂). Yields Ba(C₁₈H₁₈O₄), 2aq and CaA', 2aq

Got

Anhydride C25H200, [155°] Prisms Iso-butyry ! derivative [65°] Needles, Yields $Ba(C_{15}H_{19}O_4)_2$ 2aq, sl. sol water CaA', 2aq, and AgA'

β-0xy-phenyl-n-valeric acid C-H₂CH₂CH₂CH₂CH(OH) CH₂CO₂H [131°] Got by boiling \$\text{styryl-propionic acid with NaOHAq}\$ (Fittig, \$B\$ 24, 84) Prisms

β Oxy-phenyl-valeric acid [153°] CH, CH(OH) CH(CH,Ph) CO,H by reducing benzyl aceto acetic ether (Ehrlich, B 8, 1036, A 187, 26) Needles (from benzene)

 $-BaA'_2 2aq -Zn(OH)A' -Cu(OH)A'$

γ-Oxy-α-phenyl-valeric acid CH₂ CH(OH) CH₂ CHPh CO₂H Formed from a-phenyl-B acetyl propionic acid by reduction with sodium amalgam (Weltner, B 17, 73) The free acid at once forms the oily anhydride $C_{11}H_{12}O_2$ - $Ca(C_{11}H_{12}O_3)_2$ aq crystalline

γ-Oxy-γ phenyl-isovaleric acid The only lactone C₆H₅ CH<0 CO CH₂ 15 made by warming γ-bromo γ phenyl isovaleric acid with aqueous Na₂CO₂ (Fittig a Liebmann, A 255, 271) It yields Ba(C₁₁H₁₂O₃)₂ Oxy-phenyl-valeric acid Methyl deriva-

tive C₆H₄(OMe) CH₂ CH₂ CH₂ CH₂ CO₂H Got by reducing C₆H₄(OMe) C₄H₆ CO₂H with sodium-amalgam (Perkin, C J 39, 438) —Oil —BaA'₂ Di-oxy-phenyl-valeric acid Methylene

derivative C₁₂H₁₁O₄, is CH₂O₂O₂H CH₂O₄CH₂CH₂CH₂CO₂H Piperhydrome acid [96°] Made by reducing (8) hydropiperic acid with sodium amalgam (Fittig a Buri, A 216, 178) Thin tables (from alcohol) — CaA'₂ aq v sl sol cold water

Di-oxy-phenyl-valeric acid C₆H₅ CH(OH) CH₂ CH(CO₂H) CH(OH) CH₃ The oily anhydride of this acid is got by reducing phenacyl-acetoacetic ether (Wellner, B 17, 69)

Tri-oxy-phenyl-valeric acid Methylene derivative

CH₂O₂ C₆H₃ CH₂ CH(OH) CH₂ CH₂ CO₂H [95°] Made by reducing with sodium amalgam the acid CH₂O₂O₆H₈ CH₂ CO CH₂ CH₂ CO₂H (Weinstein, A 227, 38) Crystals, m sol hot water Yields an oily lactone -BaA'2 -AgA' flocculent pp

Tri-ppy-oxy di phenyl-valeric acid

methyl derivative

C.H. (OMe) CH(OH) CH, CH(CO.H) CH, C.H. OMe The lactone [83°] is got by the action of sodiumamalgam on its bromo derivative [136°], which is formed by dissolving di bromo di p methoxydi-phenyl-valeric acid in HOAc (Fittig a Politis, A 255, 305) It yields a gummy Ba salt

Tetra-oxy-phenyl-valeric acid Methylene

derivative

CH₂O₂C₂H₂CH₂CH(OH) CH(OH) CH. CO₂H [123°] Made by oxidising (a) hydropiperic acid with KMnO₄ at 0° (Regel, B 20, 415) Slender crystals —BaA'₂ —AgA' needles Anhydride C₁₁H₁₂O₅ [1045°] Crystals.

An isomeric acid

CH₂O₂O₃H₃CH₂CH₂CH(OH) CH(OH) CO₃H [165°], formed by oxidising (3) hydropiperic acid, yields the salts CaA', aq and AgA

Reference -TETRA - BROMO - ONY PHENYL-VALE-

RIC ACID

c OXY-PHTHALIC ACID C.H. (OH) (CO.H).
2 3] [0 200°] S 20 at 17° Obtained by [1 2 3] potash fusion from its methyl derivative (Jacob

sen, B 16, 1965), and from c sulpho phthalic acid (Stokes, Am 6, 282) Got also from camido-phthalic acid (Bernthsen, B 20, 937). Prisms (from water), v sol alcohol and ether Coloured red by FeCl, Forms a fluorescen Coloured red by FeCl, Forms a fluorescen when heated with resoroin —KHA" needles — Ag₂A" pp, sl sol hot water

 $Anhydride C_8H_8(OH) < \stackrel{CO}{CO} > O$ [c 148°]

Formed by heating the acid

Methyl derivative C₆H₃(OMe)(CO.H)₂. 0°] Formed by oxidation of c methoxytoluic scid with KMnO. Minute prisms

Anhydride of the methyl derivative

C.H.(OMe)C.O., [87°] Needles (by sublimation)

1.0xy-phthalic acid C.H.,(OH)(CO.H),[1 3 4]

[185°] (Rée), [205°] (Claus) S 3 at 10°

Formation—1 From 1-amido phthalic acid

FORMATION 1070

by the diazo reaction (Baeyer, B 10, 124, 1079) 2 By oxidising a methoxy o toluic acid with potassium permanganate, and heating the resulting C₀H₃(OMe)(CO₂H)₂ with hydrochloric acid (Schall, B 12, 816) —3 By potash fusion from $C_0H_3(SO_2NH_2)(CO_2H)_{22}$ which is got by oxidising [3 4 1] and [5 2 1] $O_0H_3Me(SO_2NH_2)(CO_2H)$ (Jacobsen, B 14, 42) —4 By fusing z sulpho phtha lic acid with NaOH (Graebe a Rée, C J 49, 524, P. 10. 1420, 1620) B 18, 1130, 1630) -5 By fusing di chloro-(α) naphthoquinone sulphonic acid with potash (Claus, J pr [2] 37, 194)—6 By fusing dinitro naphthol sulphonic acid with potash (Ree, A 233, 230)

Properties - Needles, sl sol cold water, sol alcohol and ether Gives a yellowish red colour Dilute HCl at 180° forms m oxy with FeCl₃ benzoic acid Gives the fluorescein reaction with resorcin at 200° -Ag₂A" tufts of needles

Methyl ether Me₂A" $[102^{\circ}]$ Plates Anhydride C,H,O, [165°] Made by heating the acid

Methyl derivative CoH₃(OMe)(CO H). [138°_144°] Needles Forms on heating an

Total of nearing an anhydrde [93°]—Ag₂C₈H₉O₃ curdy pp s **0xy-isophthalic** and C₈H₄(0H)(CO,H)₂ [1 3 5] [288° cor] S 0305 at 5°, 19 at 99° Made by fusing s sulpho isophthalic acid with potash (Heine, B 13, 491, Lonnies, B 13, 705) Got also from rufigallic acid by potash fusion (Schreder, M 1, 437), and by the action of nitrous acid on s-amido isophthalic acid (Beyer, J pr [2] 25, 515) Needles (containing 2aq), ▼ sol hot water, alcohol, and ether $-BaA'' 3aq - Cu_s(C_sH_2O_s)_2 4aq -Ag_2A'' - AgHA''$ needles

 $M_{\rm o}A''$ [160°] Needles ${\rm Ct_2}A''$ [103°] Prisms acid ${\rm C_6}{\rm H_3}({\rm OH})({\rm CO_2H})_2$ at 100°, 14 at 24° Di-methyl ether Me A" Di-ethyl ether Et₂A" c-Oxy-isophthalic [1 2 6] [239°] S 8 at 100°

Formation —1 Obtained by potash fusion from (2,1,6) aldehydo oxy benzoic acid (Tiemann a Reimer, B 10, 1562), and also from the acid [1 2 6] C₂H₂(SO₂NH₂)(CO₂H)₂ (Jacobsen, B 11, 902) —2 From (1,2,6) methoxy-tolure acid by oxidising with KMnO₄, and heating the resulting C₆H₄(OMe)(CO₂H)₂ with HCl at 160° (Schall, B 12, 826) —3 In small quantity, in the preparation of the following isomeride, by the action of CCl, and KOH on salicylic acid (Hasse, B 10, 2185) —4 By oxidising a naphthol with CrO, and HOAc (Miller, A 208, 247) —5 From camido isophthalic ether (M)

Properties - Needles (containing aq), v sol.

alcohol and ether Melts at 244° after drying at 100° (T a R) Coloured cherry red by FeCl. Forms salicylic acid when strongly heated Its solutions exhibit bluish violet fluorescence—
AgA" minute plates—EtA" oil.

Mono-methyl ether

 $C_0H_3(OH)(CO_2H)(CO_2Me)$ [135°] Made from 1300 H. (ONa) CO₂CH, by heating with CO₂ at 150° under pressure (Hahle, J pr [2] 44, 6) Grouped needles, which melt under water Coloured red by FeCl, Gives NaA' as colourless needles

Methyl derivative C₆H₃(OMe)(CO₂H)₂ [218°] Prisms, sol hot water

2 Oxy 1sophthalic acid $C_6H_3(OH)(CO_2H)_2$ [1 2 4] [306°] S 02 at 10°, 625 at 100°

Formation -1 By potash fusion from (2,1,4)and (4,1,2) aldehydo oxy benzoic acid (Tiemann a Reimer, B 10, 1562), from m xyienol (Jacob sen, B 11, 377), from m xylene sulphonic acid (Remsen, B 11, 580), from C₅H₃(SO NH₂)(CO₂H)₂ (Remsen, Am 1, 131), and from benzone acid (Barth, M 3, 803) —2 By the action of KOH, dilute alcohol, and CCl, on salicylic acid (Hasse) 3 By heating C₂H₄(ONa) CO₂Na [1 2] or [1 4] in a current of CO (Ost, J pr [2] 14, 93, 15, 301, Kupferberg, J pr [2] 16, 428)

Preparation -Amixture of C. H. ONa (3 mols) and C₈H₂OK (1 mol) is heated in a current of CO₂ at 300° The yield is 30 p c of the phenol

used (Ost)

Properties - Needles, sl sol water, insol chloroform Not volatile with steam Its aqueous solution is coloured cherry red by FeCl, salicylic acid and phenol when distilled yieldstri bromo phenol on heating —Na A"aq — Ca₁(C₄H₄O₅)₂ 5aq — CdA"5½aq — Ag.A" — AgHA" needles

Methylether Me, A" [96°]

Mono ethylether

 $C_6H_3(OH)(CO_2H)(CO\ Ft)\ [4\ 3\ 1]$ [195°] Made from [4\ 1] $C_6H_4(ONa)\ CO_2Et$ and CO_3 at 170° under pressure (Hahle, J pr [2] 44, 12) clinic leaflets

Di ethyl ether Et,A" [52°] Phenyl ethyl ether

C₈H₃(OH)(CO₂Ph)(CO Et) [4 3 1] from HEtA", phenol, and POCl₃ (H)

Amide C₆H₃(OH)(CONH₂)₂ [250°]

Methyl derivative C.H.O. [261°]

Hexahydride Oxy isophthalic acıd CH, CH, C(OH)(CO H) Formed by saponin-CH₂ CH(CO₂H) CH₂cation of its semi nitrile [130°-140°] which is the product of the union of prussic acid with 2186) Nodules (from alcohol) -Ag2A"

Di oxy phthalic acid Methyl derivative C_eH₂(OMe)(OH)(CO_.H)₂ Normethylhemipu acid [225°] (Wegscheider, M 3, 378) Made by warming hemipic acid with cone HIAq (Liechti, A Suppl 7, 151, Beckett a Wright, C J 29, Nodules (containing 2aq) Melts at 150°-155° when hydrated V sol water and alcohol Coloured blue by FeCl, Yields protocatechuic acid when fused with potash The anhydride acid when fused with potash C.H.O. 2aq forms crystals [148°] -KHA" aq

Di-methyl derivative v Hemipic Acid Methylene derivative **CH₂O₂.C₂H˙₂(CO₂H)₂. [175°]** Hydrastic acid.

Got by the action of boiling rotash on the methylimide [233°] which is obtained by oxidising hydrastinic acid (Freund a. Lachmann, B 22,

35) Needles (from Aq) —NMeH,A' [224°] Di-oxy phthalic acid Hexahydride Hexahydride C₈H ₂O₆ [180°] Got by the action of baryta on 'bromo malophthalic' acid (Baeyer, A 166, 855) Prisms (containing 2aq), v sol water -PbA" aq needles

Reference -- OXYTEREPHTHALIC ACID

(a) OXY-ISOPHTHALIC ALDEHYDE

C₆H₃(OH)(CHO)₂[4 3 1] [108°] Formed by boiling p oxy benzoic aldehyde with chloroform and NaOHAq, and also, together with the (β) isomeride, from salicylic aldehyde in like manner (Voswinckel, B 15, 2021) Needles, sol. ether, sl sol water, almost insol ligroin

(β) Oxy-isophthalic aldehyde $C_6H_3(OH)(CHO)_2$ [2 3 1] [88°] Made as above Needles (from water), v sol ligroin Yields

c oxy isophthalic acid on fusion with potash Di oxy-isophthalic aldehyde

 $C_6H_2(OH)_2(CHO)_2$ Resorcylic aramenyo $C_6H_2(OH)_2(CHO)_2$ Resorcylic aramenyo $C_6H_2(OH)_2(CHO)_2$ Resorcylic aramenyo $C_6H_2(OH)_2(OH)_2$ Nade by the action of chloroform and NaOHAq on resorcin (Tiemann a Lewy, B 10, 2212 . 13, 2368) Needles (from hot water) With alcoholic aniline it yields yellow crystals Phenyl hydrazine acetate forms $C_8H_2(OH)_2(CHO)_2$ [o 230°] (Rudolph, A 248, 105) Yields a dioxim [209°] (Marcus, B 24, 3652)

Methyl derivatives $C_{\rm e}H_2({\rm OMe})({\rm OH})({\rm CHO})_2$ Two isomerides, [179°] and [89°], are formed from [1 3] C.H. (OMe) (OH),

chloroform, and NaOHAq

OXY-PHTHALIDE CsH4O, 26.

 $C_0H_3(OH) < CO^2>O$ [222°] Got by reducing oxyphthalimide with tin and HCl, treating with nitrous acid, and heating the resulting nitroso oxy phthalidine with NaOHAq (Graebe a Rée, C J 49, 526) Prisms or needles, sl sol ether

OXY-PHTHALIMIDE C,H,(OH) CO>NH

or $C_{\mathfrak{s}}H_{\mathfrak{s}}(OH) < \stackrel{C(NH)}{CO} \longrightarrow O$ [290°] Formed by saturating a oxy phthalic acid with NH, (Rée, A 233, 232, C J 49, 525) Yellow crystals, sl. sol ether When reduced by tin and HCl it yields a product from which a nitroso compound [170°] may be prepared

OXY-DIPHTHALYL C16H8O3 26

C₆H₃OH [above 374°] \co`o o'co/

Made by heating phthalide with 2-oxy phthalic anhydride and NaOAc at 200° (Graebe a Guye, A 233, 244) Needles (from HOAc)
A d1-oxy-diphthalyl [250°] appears to be

formed by dissolving di-chloro diphthalyl in alcoholic potash (Ador, A 164, 245)

DI-OXY-PROPANE v PROPYLENE GLYCOL

DI-OXY PROPANE TRI-CARBOXYLIC ACID $C_sH_s(OH)_s(CO_2H)_s$ Formed by exidation of isosaccharin with HNO_s (Kiliani, B 18, 638) Colourless syrup By HI it is reduced to glutaric acid $C_sH_s(CO_2H)_x$ —A"₂H_sCa small prisms

An isomeric acid, formed by boiling chlorecitric acid with lime, forms the salts Ca,A", 9aq, Ba₂A'''₂5aq, and Cd₂C₆H₄O₂8aq (Pavolleck, A. 178, 157) The same acid, yielding Ca₂A'''₂10aq, occurs in best toot juice (Lippmann, B 16,

Tri-oxy-propane tri carboxylic acid C,H,O, s.s. CO₂H CH(OH) CH(OH) C(OH)(CO₂H)₂ Got by oxidising mannite with alkaline KMnO₄(Pabst, J. 1880, 611) Yields a soluble NH, salt

OXY-PROPANE PHOSPHONIC ACID

C,H,PO, te CHEt(OH) PO(OH)2 [162° Formed from propionic aldehyde and PCl, followed by water (Fossek, M 7, 29) Plates, v sol water —CaA"

OXY-PROPANE SULPHONIC ACID

C₂H₆(OH)(SO₂H) Formed from n propyl alcohol and SO, and also by boiling allyl alcohol with aqueous KHSO, (Max Müller, B 6, 1441) The same, or an isomeric acid, is got from propylene oxide and NaHSO, (Erlenmeyer, A 158, 260) The K salt crystallises in small needles

Oxy-propane disulphonic acid CH(OH)(OH₂SO₃H)₂. Formed by boiling glycerin dichlorhydrin with aqueous K2SO, (Schauffelen, 4 148, 111) and, in like manner, from epichlor hydrin (Pazschke, J pr [2] 1, 86, Z [2] 5, 61 δ) Syrup.—K,A" 2aq trimetric octahedra a b c = 41 48 1—BaA' 2aq m sol water—PbA" 2aq —Ag,A" crystals, v sol alcohol

Reference - CHLORO-OXY-PROPANE SULPHONIC

TRI-OXY-PROPENYL-BENZENE Tri

methyl derivative

[1245]C.H.(OMe), CH CHMe This is the constitution of asarone (q v) (Eykmann, B 22, 3172). OXY-PROPENYL-BENZOIC ACID

 $C_eH_s(O_3H_5)(OH)CO_2H$ [4 2 1] Propenyl-salicylic acid [146°] Formed from oxylsopropyl-salicylic acid C₂H₂(CMe₂OH)(OH)CO₂H, by elimination of H₂O by warming with dilute HČl White slender needles V sol. alcohol, ether, and CS₂, sl sol water Sublimable Volatile with steam Gives a deep reddish-violet colouration with Fe₂Cl₂. By sodium amalgam it is reduced to oxy-cuminic acid C₆H₈Pr(ŎH)CO₂H [4 2 1]

Salts—A'Ag sparingly soluble white crystalline pp—A'₂Cu 2aq small green crystals, nearly insol water

[230°] Formed by Folymeride $(O_{10}H_{10}O)_x$ [280°] Formed by boiling oxy-properly benzoic acid with strong Small white crystals M sol hot acetic acid, alcohol, and ether, insol water and CS2 Gives a deep bluish-violet colouration with Not volatile with steam — (CuA" 12aq)x. —(AgA')_x white pp (Heymann a Königs, **B**. 19, 3818, 20, 2890)

OXY-PROPIONAMIDINE

CH, OH(OH) C(NH) NH₂.

The hydrochloride B'HCl is formed from (OH, CH(OH) C(NH) OC, H₁₁) HCl, and alcoholoc NH, (Pinner, B 28, 2947) "Needles, converted by AgNO, into B'HNO, [84°], v sol water OXY-PROPIONIC ACID v LACTIC ACID and

HYDRAGBYLIC ACID V. also Bromo-, Chloro-,

and Iodo-, Oxy-Propionic ACIDS

Di-oxy-propionic acid v GLYCERIC, GLYCXYLIC,

PYRUVIC, and GLYCIDIC ACIDS

a-OXY-PROPIONIC ORTHALDEHYDE Tramethyl derivative C_eH₁₄O_e is CH₂ OH(OMe) CH(OMe)₂. (148°) SG 2 948 Formed by heating acrolein (2 vols) with methyl alcohol (6 vols) and HOAc (1 vol) at 100° (Alsberg, J 1864, 495). Laguid, with pleasant smell, al sol water.

Tri-ethyl derivative (186°) SG 15.90.

OXY-PROPIONIC IMIDO ISOAMYL ETHER CH, CH(OH) C(NH) OC,H₁₁ The hydro-chloride B'HCl [69°], forme! by the action of HCl gas on a solution of aldehyde cyanhydrin in isoamyl alcohol, crystallises in thin needles The homologous CH, CH(OH) C(NH,Cl) OC,H. also melts at 69° and gradually decomposes form ing lactamide and ammonium chloride (Pinner, B 23, 2947

OXYPROPYL-AMIDO BENZOIC ACID

 $C_6H_3(CMe_2OH)(NH_2)CO_2H$ [4 2 1] [158°] Made by reduction of nitro oxypropyl-benzoic acid with FeSO, and ammonia (Widman, B 19, 271) Exhibits blue fluorescence in ethereal solution

Acetyl derivative

C₆H₅(C₅H₆ OH)(NHAc)CO₂H [174°] Trimetrio tables, v sol hot alcohol

Oxypropyl amido-benzoic acid

 $C_6H_8(CMe_2OH)(NH_2)(CO_2H)$ [4 3 1] Made by reducing the corresponding nitro acid (Widman, B 16, 2570, 17, 1305) Prisms, v sol alcohol, v sl sol ether With ClCO Et it forms C₀H₂(CMe₂OH)(NH CO₂Et) CO.H [167°] and C₂H₂₈N₂O₂ [above 300°] which is converted by H₂SO₄ into CO(NH C₂H₂(CMe₂OH)(CO.H))₂

Acetyl derivative Crystalline

a OXY PROPYLAMINE CH₃ CH(OH) CH NH₂ Amido iso propyl alcohol (1766) Formed from allylamine and H2SO4, followed by water (Liebermann a Paal, B 16, 531) Needles

Benzoyl derivative CH, CH(OBz) CH₂NH₂ Got by boiling bromopropyl benzamide with HBrAq Oil, v sol water Converted into CH, CH(OBz) CH OH by nitrous acid Boiling NaOHAq converts it into the isomeric CH₈CH(OH) CH₂NHBz [93°] (Hirsch, B 23, 970) — $C_{10}H_{18}NO_{2}HBr$ [133°] Needles — $B'C_{6}H_{3}N_{3}O_{7}$ [189°] Needles — B'2H2PtCl6 yellow needles (from water)

β-0xy-propylamine CH₂(OH) CH₂ CH₂NH₂ Formed by heating bromo propyl phthalimide with dilute (12) H₂SO, for 5 hours at 200° (Gabriel, B 21, 2672) — B'.H₂PtCl₄. yellow plates —B'HAuCl₄ plates

Sulphurie acid derivative CH₂(O SO₂H) CH, CH₂NH, [221°] Formed from \$\beta\$ bromo propylamine hydrobromide and aqueous Ag₂SO₄ at 100° (Gabriel a Lauer, B 23, 91) Prisms (from warm water) Indifferent body

Bensoyl derivative NH₂ C₃H₆ OBz Liquid, v sol water Formed from phenylpentoxazoline and HBr (Gabriel a Elfeldt, B 24, 3216) Yields B'HBr [135°], B'₂H₂PtCl₃ [205°] and B'C₃H₃N₃O, [178°]

Pheny l derivative PhO C₂H₄ NH₂ (242°) Got from phenoxy propyl phthalamic acid and HCl (Lohmann, B 24, 2684) Yields B'HCl [168°] crystallising in shining plates, and Pho C.H. NHBz [118°] Pho C.H. NH CO NH, [114°]. Cyanic acid forms

Oxy-di-propyl amine (C,H₂OH)(C₂H₂)NH (175°) [80°] S G 12 9018 Prepared by heating propyl-allyl amine with H₂SO₄ and pouring the product into water (Liebermann a Paal, B. 16, 581) Needles B',H,PtCl, 2sq efflorescent Oxy-tri-propyl amine (C,H,OH)N(C,H,)

Got by heating di-propyl-allyl-amine

H.SO, and pouring the product into water (L a.

P)—B',H,PtCl₆
OXY PROPYL AMYL AMINE C,H,,NO 16 (C,H,0H)(C,H,1)NH (c 200°) [c 2°] Formed by heating allyleamyl amine with H₂SO₄ and pouring the product into water (Liebermann a. Baal, B 16, 531) Solidifies to long fine needles

Oxy propyl di isoamyl-amine $(C_8H_{11})_2N(C_8H_6OH)$ (243°) Formed from propylene chlorhydrin and dı ısoamylamıne (Louise, A Ch [6] 13, 433) Oil, sl sol water Inactive to light -B'2H2PtCl, orange crystals The acetyl and benzoyl derivatives form crystal-line xalates, the latter being C₂₀H₂₈NO₂H₂C₂O₄

OXY PROPYL-BENZENE v. PROPYL PHENOL

and PHENYL PROPYL ALCOHOL.

Di-oxy propyl benzene CH, CH(OĤ) ĈH(OH) C,H, [53°] Made from phenyl propylene bromide by successive treatment with KOAc and alcoholic potash (Zincke, B 17, 709) Tables (from ether ligroin), v e sol water A more sparingly soluble isomeride [93°], made from phenyl propylene bromide by boiling with aqueous K₂CO₂, crystallises from ether in monoclinic tables

Tri-oxy propyl-benzene v Propyl Pyro-

GALLOL

Tetra-oxy-propyl-benzene Methylene derivative CH2(OH) CH(OH) CH2 C6H3O2CH2 [83°] Formed from safrol and dilute KMnO, at 75° (Tiemann, B 24, 2881) White needles, v. sol boiling water and ether Yields piperonal, piperonylic acid, and CHO, C.H, CH. CO.H on further oxidation Phenyl cyanate forms further oxidation Phenyl cyanate CH₂O₂ C₆H₃ CH C₆H₄(O CO NHPh)₂ [127°]

Acetyl derivative

CH₂O₂C₂H₃CH₄CH₄C₂H₃(OAc)₂ (240° at 18 mm) OXY PROPYL-BENZENE SULPHONIC SULPHONIC

Got from cumene ACID Me C(OH) C₆H₄ SO₃H p-sulphonic acid, KOH and KMnO, (R Meyer, **4** 219, 302)

Salts -KA' -BaA', Splits off H₂O at 140° -PbA'₂ Splits off 2H₂O at 110°, probably forming lead propenyl benzene sulphonate

Reaction -PCl, followed by ammonia forms the amide of propenyl benzene sulphonic acid

[152°]

OXY o-ISOPROPYL BENZOIC ACID

 $CMe_2(OH) C_9H_4 CO_2H$ The salt KA' [197°] is formed by the action of cone KOHAq on dimethyl-phthalide (Wislicenus, A 248, 59) The tree acid is unstable, at once forming di methyl-

phthalide [68°]

Oxy-p isopropyl-benzoic acid CMe₂(OH) C₆H₄ CO₂H Formed [156°] oxidising cuminic acid, or cymene, with alkaline KMnO, (R Meyer, B 11, 1283, 1790, A 219, 248, Remsen a Emerson, A C J 1, 267, Widman, B 19, 583) Thin triclinic prisms (from water), v sol alcohol and ether Gives no colour with FeCl, Yields terephthalic and acetyl benzoic acids on oxidation by CrO, Boiling HClAq forms two isomeric propenyl-benzoic acids. — BaA', aq — CaA', 2 aq — CuA', 3aq — AgA' aq crystalline pp

An isomeric or identical acid is got by boiling bromo-propyl benzoic acid with alcoholic potash

(Czumpelik, B. 8, 478)

Isomerides v Oxy-cuminic acids. Di-oxy-isopropyl-benzoic acid C.H.(CMe,OH)(OH) CO.H [1 2.4] [178*]. Formed by the action of nitrous acid on oxyamido isopropyl benzoic acid (Widman, B 17, 722) Crystals (from water), v sol alcohol and Coloured dark brown by FeCl.

Di oxy-isopropyl benzoic acid

 $C_{\mathbf{g}}\mathbf{H}_{\mathbf{g}}(\mathbf{CMe_{2}OH})(\mathbf{OH})\ \mathbf{CO_{2}H}\ [1\ 3\ 4]$ [130°-135°]. Formed by oxidising carvacryl sulphuric and with alkaline KMnO₄ (Heymann a Konigs, B. 19, 3310) Flat needles (from water), v e sol alcohol—CuA', aq—AgA' needles

DI-OXY-DI-ISOPROPYL-DI CARBOXY DI-PHENYL-ALLOPHANIC ETHER C24H28N2O9 2.e. $N(CO_2Et)C_6H_8(CMe_2OH)CO_2H$ fabove 300°1. CÒ NH C₆H₂(CMe₂OH) CO₂H Formed, with CO(NH C₆H₅(CMe₂OH) CO₂H)₂ and CO₂Et NH C₄H₄(CMe₅OH) CO₂H [167°], by the action of ClCO₂Et on oxy amido-isopropylbenzoic acid (Widman, B 17, 1306) Tables (from HOAc), almost insol water

OXY-PROPYLENE-DIAMINE CsH10N2O + 6. CH(OH)(CH₂NH₂)₂ Formed from glycerin di-chlorhydrin and alcoholic NH₂ (Claus, A 168, 36) —B"H2PtCl

OXY-PROPYLENE-TETRA METHYL-DI-AMINE C₂H₅(OH)(NMe₂)₂ (170°-185°) Formed by heating s dichlorhydrin with NMe2H (Berend, B 17, 510) Liquid, v sol water

Bensoyl derivative Crystalline

OXY PROPYL-ETHYL-AMINE v. ETHYL-OXY-PROPYL AMINE

OXY-PROPYL-MALONIC ACID

CO₂H CH(CH₂.CHMeOH) CO₂H The free acid at once splits off water, leaving the lactonic acid The salts BaC, H,O,, CaA", and Ag,A" may, however, be prepared

Lactonic acid C₆H₈O₄ Got by combining allyl malonic acid with HBr, and boiling the product with water (Hjelt, B 15, 621, A 216, 53) Syrap, v sol water, sl sol ether Yields Ba(C₆H O₄)₂ crystallising in soluble plates

D1-oxy-propyl-malonic acid (CO2H)2.CH CH2.CH(OH) CH2OH The free acid in aqueous solution remains unchanged at 15°. but at 100° it splits off water, forming a lactonic

acid whose barium salt is (C₆H₂O₅)₂Ba Salts —BaA" Got by boiling di-bromo-Salts -BaA" propyl malonic acid with baryta (Hjelt, A 216,

58) -Ag₂A" flocculent pp

Di oxy di propyl-malonic acid

(CH₃ CH(OH) CH₂)₂C(CO₂H)₂. Dilactone C₉H₁₂O₄ [1069] Obtained from di allyl malonic acid by evaporating with cone HBrAq (Hjelt) Thin plates (from alcohol), long needles (from water), or trimetric crystals (from conc HBrAq) abc = 611 94 baryta water forms (C,H,O),C(CO,),Ba, which on heating splits up into BaCO, and the neutral lactone C,H,O CH CH, CHMe

Reference - DI - BROMO - DI - ONY - DI - PROPYL -MALONIC ACID

DI-OXY-ISOPROPYL-TRIMETHYLENE socalled CHPr CH OH? (126°) S 10 Formed from isobutyric aldehyde and ethylene glycol by heating in a sealed tube (Lochert, Bl [2] 48, Liquid, lighter than water, v sol alcohol and ether Decomposed by water at 100° into its constituents. Bromine yields a heavy oil C₂H₂Br CH(CH OH)₂ (c 187°).

a OXY-p-PROPYL-PHENYL-ACETIC ACID C₁₁H₁₄O₂ te C₆H₄(C₅H₇) CH(OH) CO₂H [158°]. S 19 at 21° Formed from cuminic aldehyde, HCy, and HCl (Raab, B 8, 1148, Plochl, B 14, 1316) Small needles (from water) — BaA', 4aq — PbA', —AgA' stellate needles OXY ISOPROPYL-DIPHENYLENE-KETONE

CARBOXYLIC ACID C, H,O, 10

 $CO < C_{0}H_{2}(CM_{0}OH) CO_{2}H \begin{bmatrix} 1 & 6 \\ 5 & 2 \end{bmatrix}$. [190°]

Formed by oxidising retene quinone with alkaline KMnO, (Bamberger a Hooker, B 18, 1030, 1750, A 229, 150) Yellow plates, sl sol cold water and ether, m sol alcohol —BaA'₂ aq —CuA'₂— AgA' yellow flocculent pp

Oxim Not melted at 270° TRI OXY-TRI-PROPYL-PHOSPHINE

Hydrate PH(OH)(CH(OH) C₂H₃)₃ Formed by the action of conc KOHAq upon (C₃H₇O)₃PHI, which is got, together with the crystalline oxypropylo rodide (C₈H₇O),PI by dissolving PH₄I in propionic aldehyde at 0° (De Girard, A Ch [6] 2, 24) Syrup, sl sol water

OXY PROPYL PHTHALIMIDE C,H,NO, se C₈H₄ C₂O₂ N CH₂ CH, CH₂OH Formed from bromo propyl phthalimide and hot conc KOHAq (Gabriel a Lauer, B 23,87) Needles (from Aq)

Phenyl derivative C.H. C.O. N C.H.OPh Formed from the bromo propyl- deriva tive of phenol and potassium phthalimide at 220° (Lohmann, B 24, 2633) Needles, converted by KOH into PhO C3H6 NH CO C6H4 CO2Et

[134°] a white crystalline powder OXY PROPYL-PIPERIDINE

C₃H₁₀N C₃H₆ OH So called 'piperpropylalkine' (194°) SG 2 947, 2 936 VD 479 (obs) Made from piperidine and propylene chlorhydrin (Ladenburg, B 14, 1880, 2407, 15, 1144, Laun, B 17, 680) Liquid, sol water —B'HAuCl, -B',HPtCl, —Mandelate dilute HCl form dilute HCl forms C16H2NO3, which gives B'HAuCl

Acetyl derivative C8H18NO -B'HAuCl Bensoyl derivative C, H, N C, H, OBz -B'HAuCl, -B'C, H,N,O, yellow powder

Oxy-propyl-piperidine C₃H₃(CH₂ CH(OH) CH₃)NH So called '(a)-propectly methylalkine' [47°] (225°) Got by C₅H₅(ČH₂ CH(OH) CH₅)NH reducing the corresponding oxypropyl pyridine with sodium and alcohol (Ladenburg, B 22, Crystalline, v sol water, alcohol, and Yields an oily nitrosamine —B'₂H₂PtCl₆ ether [149°] Small crystals (from alcohol)

Oxy-propyl-piperidine C_bH_p(CH(OH)Et)NH [100°] Got by reducing (a) pyridyl ethyl ketone in amyl alcohol with sodium (Engler a Bauer, B 24, 2533) Needles Probably identical with the \(\psi \) conhydrin in Consum maculatum

Dioxypropyl-piperidine CoH1,NO2 Made by heating piperidine with glycerin chlorhydrin (Roth, B 15, 1150) Silky plates — B'HBr — B'HAuCl, yellow needles

OXY-PROPYL-PYRIDINE $C_8H_{11}NO$ C₅H₄(CH₂ CH₂ CH₂OH)N So called '(a) lutdylalkme' (c 130° at 17 mm) Formed from (a) ethyl pyridine and formic aldehyde (Ladenburg a Adam, B. 24, 1678) V sol water.—
B'HAuCl₄ [71°]—B'₂H₂PtCl₅ [142°]

Hexahydrade C₂H₁₁NO—B'HBr

Oxypropyl-pyridine C,H,(CH, CH(OH) CH,)N '(a)-proolylmethylalkine' (1760-181° at 18 mm.) Made from

(a) methyl-pyridine and acetic aldehyde (L) Liquid, al sol water - B'2H2PtCl [189°] Small tables, sl sol water

Oxy propyl-pyridine C_sH₄(CH(OH)Et)N (215°) Got, together with corvine and another body [69°], by reducing (a)-pyridyl ethyl ketone with sodium amalgam at 30°-40° (Engler a Bauer, B 24, 2532) -B'2H2PtCl6

Oxy - propyl - pyridine Tetrahydride CH₂CH_(C,H,)CO CH₂NH [57°] (274°)

Made by heating δ amido-α propyl valeric acid to 200° (Aschan, B 23, 8701) Flat snowy needles

OXY - PROPYL - PYRIDINE DIHYDRIDE CARBOXYLIC ACID v MORRHUIC ACID

(Py 3) OXY-(B 3)-ISOPROPYL-QUINOLINE OH CH C CH CH Cumostyrıl [169°] Made CPr CH CN COH by boiling the hydrochloride of phenyl o amido cumyl acrylic acid with water and a few drops of HCl for 5 hours (Widman, B 19, 264) Needles, v sol hot alcohol, sl sol hot water

Oxy - n - propyl - quinoline DihydrideCH CH C CH₂ CH₂ [134°] Formed, by intra CPr CH C NH CO molecular change, by reducing the preceding body, and also from nitro n cumyl propionic acid (Widman, B 19, 2778) Prisms (from benzene ligroin), insol water

OXY-PROPYL SUCCINIC ACID Lactonic CH, CH CH2 CH CH2 CO2H (c 260°) Formed from allyl succinic acid and conc HBrAq (Hjelt, B 16, 334) Crystals (from alcohol)

OXÝ ISOPROPYL-SULPHOBENZOIC ACID $CMe_2(OH) C_6H_3(SO_3H) CO_2H$ [1 3 4] Made by oxidising cymene sulphonic acid, an intramole cular change taking place Got also from iso cymene sulphonic acid and KMnO, (R Meyer a Boner, A 220, 8, 30, B 13, 1495, 14, 2301, Remsen, Am 8, 262) $-K_2A''$ 5aq Triclinic crystals, a b c = 6751542, $a = 131^{\circ}$ 14', $\beta = 104^{\circ}$ 26', $\gamma = 66^{\circ}$ 27' $-K_2A''$ 2aq -BaA'' aq $-K_2A''$ 2aq $-K_2A''$ 2aq 2aq An isomeric acid, got from m isocymene sul phonic acid, yields BaA" and PbA"

OXYPROPYL p-TOLUIDINE C10H15NO 1 e C₆H₄Me NH C₃H₆OH [74°] (293° cor) Formed from propylene oxide and p toluidine (Morley, C J 41, 387, B 15, 179) Needles (from light petroleum), insol water, v sol benzene and Pearly plates

ether — B'H,C,O, [151°] Pearly I (a) OXY-PYRIDINE C,H,NO ve N≪CH CH CH CH VD 28 (obs) [107°]

Formed by distilling its carboxylic acids (Konigs, B 16, 2160, 17, 590, 2391, 19, 2403, Pech mann, B 17, 2384, Weidel a Strache, M 7, 297) Dimetric needles, v e sol water and alcohol Coloured red by FeCl, Yields a di bromo-oxy pyridine [2079

Tetrahydride C.H.NO 1.e NH CO CH₂ CH₂ CH₂ [40°] (255°) Made by distilling 8 amido valerio acid (Schotten, B 21, 2285, Gabriel, B 23, 1770) Crystalline mass. Yields an acetyl derivative (238°)

(8) Oxy-pyridine C,H,NO 1.e NCHC(OH)OH [124 5°] Formed by potash fusion from pyridine sulphonic acid (Fischer a Renouf, B 17, 763, 1896) Needles, v sol water and alcohol Coloured red by FeCl.

Oxalate [175°] White needles

Acetyl derifative (210° uncor) Oil Ethyl derivative Made by ethylation, and also from bromo pyridine and alcoholic potash (Weidel a Blau, M 6, 664) $B'_{2}H_{2}PtCl_{6}$ [192°] Prisms

Methylo vodide B'MeI Needles Methylo-chloride B'MeCl Needles -B'2Me2PtCl6 Orange prisms, sl sol alcohol

(7' Oxy pyridine NH CH CH CH CO Pyridone [148°] (above 350°) S 100 at 15° Formed by heating chelidamic acid under re duced pressure at 230° or with water at 196° (Lerch, M 5, 402, Haitinger a Lieben, M 6, 300) Formed also by distilling its carboxylic acid (Ost, J pr [2] 29, 65) Small efflorescent grains (from alcohol), prisms (containing aq), or V sol water trimetric tables, abc = 55115and alcohol Melts below 100° when hydrated Converted by treatment with MeI and KOH into NMe CH CH CO, a deliquescent mass [89°] which gives $(C_6H_7NO).H_2PtCl_8$ aq $[176^\circ]$, B'MeI, and B Me_PtCl $_8$ Does not yield an acetyl de rivative

Salts - B'2H PtCl6 aq - B' H2PtCl6 2aq Efflorescent monoclinic needles [200°], converted by boiling water into B'sH2Pt2Cl10 aq- $B'HNO_3AgNO_3$ tables $-B'HgCl_2 - B'HHg_2Cl_3$

Methyl derivative N CH CH CH COMe

(191° coi) at 738 mm Formed from (γ) chloropyridine and NaOMe (H a L) Liquid, sol Changes at 220° water Alkaline in leaction into the crystalline isomeride (v supra) Gives a deep blue liquid with aqueous CuSO. HIAq converts it into (γ) oxy pyridine - B'₂H₂PtCl₆ crystals, sl sol water

Di-oxy-pyridine $C_3H_3(OH)_2N$ [c 255°] (K a G), [239°] (W a B) Formed by potash fusion from its ethyl derivatives and also from pyridine disulphonic acid (Konigs a Geigy, B 17, 1835, Weidel a Blau, M 6,651) Needles (containing laq), v sol water, sl sol alcohol Coloured red by FeCl₃—B'HCl needles

Mono ethyl derivative C, H, NO [128°] Formed, together with the di ethyl derivative, by heating dibromopyridine [111°] with alcoholic Tables, sl sol cold water -B'HNO, otash B'2H2PtCl6 red triclinic needles

Diethyl derivative C,H3(OEt),N 244°) Made as above Liquid, nearly insol water -B'.H.PtCl, yellow needles -B'HHgCl, Crystals (from HClAq)

Di-oxy-pyridine Di oxim of the dihy- $NH < C(NOH) CH_2 > CH_2$ [193°] product of the action of hydroxylamine on trimethylene cyanide (Biedermann, B 22, 2967) Yields a di acetyl derivative [127°] and a dibenzoyl derivative [180°]

[175°] Needles. Picrate Tri-oxy-pyridine C.H.NO. a.s

N < C(OH) CH > C OH [220°-230°]. Formed by boiling di-oxy amido pyridine (glutazine)

with cone HClAq (Stokes a Von Pechmann, Am 8, 384, B 19, 2701) Yellowish sandy powder, v sol hot water On evaporation of its solution it is partly converted into its anhydride. FeCl₃ gives a red colour Forms with bromine CBr, CO CBr, CONH, NH, OAc at 140° converts it into glutazine —BaA', —AgA' —B'HCl

Oxim NH CO CH2>C NOH Made by boiling tri oxy pyridine or glutazine with hydroxylamine hydrochloride hexagonal plates (containing aq), m sol hot water -B'HCl plates

Phenyl-hydrazide

NH CO CH₂ C N₂HPh [230°] Tables

Anhydride C10H8N.O5 Made by boiling glutazine with dilute H.SO, Minute flesh coloured prisms, sl sol water -BaA'24aq yellow prisms -AgHA" -B'H2SO4 -B'HCl References -DI BROMO, DI CHLORO, and DI

IODO , OXY PYRIDINE

OXY-PYRIDINE CARBOXYLIC ACID

C₅H₅N(OH) CO₂H (a) Oxypicolinic acid [267°] Made by heating di chloro oxy pyridine carb oxylic acid [282°] with HI in HOAc at 210° (Ost, J pr [2] 27, 289) Long needles (con taining aq) or short anhydrous needles, v sol hot water and alcohol, insol ether Coloured reddish brown by FeCl₂ AgNO₃ is not reduced, but gives a white pp -BaA'2 aq -CaA'2 C₅H₂N(OK) CO₂K aq groups of needles

Oxy pyridine carboxylic acid C₅H₃N(OH) CO H (β)-Picolinic acid [250°] Made by the action of HI in HOAc on chloro oxy pyridine carboxylic acid [257°] at 200° (Ost) Formed also without by products by boiling comanic acid C.H.O.(CO H) with NH,Aq (Ost, J pr [2] 29, 64) Glittering plates Yields oxypyridine [148°] on heating strongly — Salt BaA', 2aq small needles, m sol water

Oxy pyridine carboxylic acid C,H,N(OH) CO,H (γ) Oxy picolinic [258°] Formed by the action of tin and HClAq on chloro oxy pyridine carboxylic acid [224°] (Bellmann, J pr [2] 29, 7) Small trimetric pyramids (containing aq), sl sol water, sol conc HClAq Coloured brown by FeCl2 -BaA'₂ prisms —CaA'₂4aq needles

Oxy-pyridine carboxylic acid C₅H₃N(OH) CO H 2 e

C(OH) CH CH CO.H Oxy moothing acid Formed by heating oxy-pyridine di carboxylic (oxyquinolinic) acid with water at 195° (Königs a Geigy, B 17, 589) Formed also by the action of NH, Aq on the methyl ether of coumaic acid (v vol ii p 264), the product being saponified (Pechmann a Welsh, B 17, 2384, C J 47, 145) Needles, sl sol hot water May be sublimed PCl, yields chloro pyridine carboxylio acid, whence tin and HCl form nicotinic acid FeCl, gives a light yellow colour—PbA'224aq needles, sol hot water

Methyl derivative C₂H₃N(OMe) CO₂H

[238°] Formed by methylating the acid, and also from methyl coumalate and methylamine, the product being saponified Needles (containing aq), nearly insol cold water

Phonyl derivative C.H.N(OPh) CO.H.

[280°] Formed by the action of boiling NaOHAq on methyl coumal anilidate (loc cit) Needles Oxy-pyridine carboxylic acid

CH ≪ CH CH > C CO₂H (a) Oxy-nicotinic acid Formed by heating (a)-oxy isocincho meronic acid with HOAc and a little Ac₂O at 210° (Weidel a Strache, M 7, 295) needles (from water) Yields (a) oxy pyridine when heated -AgA' sılky needles

Oxy-pyridine dicarboxylic acid C,H,NO, 2 e N C(O₂H) CH (a) Oxyrsocrachomeronic acid Formed by oxidising (a) diquinolyl with KMnO₄ (Weidel a Strache, M 7, 293) ronic acid Vitreous crystals Gives no colour with FeCl, BaA" -Ag2A" needles, nearly insol water

Oxy-pyridine dicarboxylic acid
C,H_N(OH)(CO,H), r e
N C(CO,H) O(CO,H) CH N≪C(OH) Oxyquinolinic Formed from quinolinic acid by potashfusion (Königs a Körner, B 16, 2158) Small crystals (from dilute H₂SO₄), blackening at 254° FeCl, colours its aqueous solution red Its Ag salt yields (a) oxy-pyridine on heating-BaA'₂ 4aq needles (from hot water)

Methyl derivative C5H2N(OMe)(CO4H)2 [140°] Got by adding KMnO, to an aqueous solution of the methyl derivative of (γ) amidocarbostyril (Feer a Königs, B 18, 2398) Needles,

▼ e sol water —AgH₃A"₂ Needles (from water)
Isomeride v Chelidamic acid, vol 1 p 729 D1-oxy-pyridine carboxylic acid C6H5NO4 2 e

N COH CH COLH? Crtrazec acid Formed by heating the mono-, di-, or tri- amide of citric acid with HCl or H2SO, (Behrmann a Hofmann, B 17, 2687) Crystalline powder, nearly insol water, sl sol hot HClAq Carbonises at 300° PCl, converts it into di chloro-pyridine carboxylic acid [210°] Gives a deep blue colour with NaNO₂. Tin and HCl reduce it to tricarballylic acid -BaA', 2aq

Di-acetyl derivative Crystalline Methyl ether MeA' Plates, decomposing above 220°

Ethulether EtA' Plates

Amide C.H.2N(OH)2.CONH2 Formed by the action of conc NH3Aq on ethyl acetyl citrate and on aconitic ether (Ruhemann, C J 51, 405. B 20, 8366) Small grey crystals (from water) Di-oxy-pyridine carboxylic acid

C₅H₂N(OH)₂CO₂H Comenamic acid Di oxupicolinic acid Formed by heating hydrogen ammonium comenate at 190°, or by boiling comenic acid with NH,Aq The yield is about 45 pc of the comenic acid used (How, T E 20 [2] 255, A 80, 65, 83, 350, Ost, J pr [2] 27, 269) Tables (containing 2aq), m sol hot water and alcohol Not decomposed by boiling

NaOHAq Gives a purple colour with FeCl.

Reactions—1 Yields pyridine on distillation with zinc-dust (Lieben a Haitinger, B 16,1263)

2 Cone HIAq at 200° does not attack it, but when heated with it for two days at 270° pyrocomenamic acid (probably a di oxy-pyridine) C₃H₂NO₂ is formed This body crystallises in needles (containing aq), gives a violet colour with FeCl₂, and forms B'HBr —8 PCl₃ (8 mols) acting on the soid (1 mol) at 100° forms a product

which on treatment with tin and HClAq yields a di-oxy-methyl-pyridine C₆H, NO₂, crystallising in trimetric prisms (containing aq), and form ing the salts B'HCl and B'H2PO, PCl, and POCl, at 200° convert this 11-oxy methyl pyridine at 200° into hexa chlois methyl pyridine and C.H.Cl.N(CCl.), which is converted by boal ing water into chloro (7) oxy pyridine (a) carboxylic acid (Bellmann, J pr [2] 29,19) Excess of PCl₃ (5 mols) at 220° acting on comenamic acid in presence of POCl, forms penta and hexa chloro-methyl pyridine, and other bodies, whence water produces chloro (γ)-oxy pyridine (a) carb. oxylic acid and chloro cyamic acid CaH C.NO. which crystallises in needles [186°], and gives a blue colour with FeCl₃ Chlorocyamic acid yields the salts AgA' and BaA'2 aq -4 Ammonium comenamate forms, among other products, on distillation, a very poisonous base called 'Oxycomazine' $C_{10}H_1N_1O$ (Krippendorff, J pr [2] 32, 153) The base crystallises from alcohol in four sided prisms, S 0035 at 20° tions in dilute acids show green fluorescence, and in strong acids a blue fluorescence Tin and HCl reduce it to oxy amido pyridine Oxycomazine forms the following salts BH2Cl [c 265°], B'H₂PtCl₈, B'H₂SO, 3aq, [c 295'], and C₁₀H₈AgN₂O -5 KMnO, oxidises comenamic acid to tri oxy pyridine carboxylic acid

Salts — NH,A' very small grains —
BaC,H,NO,aq pp —BaA', 2aq crystalline
Ethylether EtA' [205] Needles (con-

taining aq), sol hot water (Reibstein, J pr [2] 24, 284) Yields Ba(C.H.NO.), 2aq and EtA'HClaq, both crystalline When heated with AcCl it yields an anhydride C,H,NO, [261°] and two derivatives, C,H,N(OH)(OAc) CO,Et [152°] and C, H, N(OAc), CO, Et [38°] BrCl forms $\dot{\mathbf{C}}_{s}\mathbf{H}_{z}\dot{\mathbf{N}}(\mathbf{OBz})_{z}\dot{\mathbf{CO}}_{z}\dot{\mathbf{E}}\mathbf{t}$ [102°]

Di-oxy-pyridine carboxylic acid C_sH_sNO₄ Oximido comanic acid Made from comanio acid and hydroxylamine (Ost, J pr [2] 29, 378)
Small needles, decomposing at 200° Reduced by tin and HCl to (β) oxy picolinic acid

Di oxy pyridinė dicarboxylic acid Ethy! derivative N\sigma_{C(OH)}^{C(OEt)} \begin{picture}{c(CO,H)} \cong CH & [182°]. Formed by the action of NaOHAq on the monoethyl ether EtHA" [160°], which is made by treating ethoxy (a) pyrone dicarboxylic ether with NH, Aq (Guthzeit a Dressel, B 22, 1427, 262, 104) Needles (containing aq) HClAq at 140° forms glutaconic acid [134°] PCl, in POCl, at 250° gives di chloro pyridine dicarboxylic acid [230°] whence Et, A" [76°] and,

by treatment with HI, pyridine dicarboxylic acid
[322°] may be prepared —Ag₂A"

Mono-ethyl ether

CH C(OEt) C(CO.Et) N [160°]. Needles Yields AgA' and an acetyl derivative C12H12NO, [100°].

Di-ethyl ether Et2A' [819] Tri-oxy-pyridine carboxylic acid C.H.NO. Tri-oxy-picolinic acid Oxy comenamic acid. Formed, in small quantity, by oxidising comer amic acid with potassium permanganate and H₂SO₄ in the cold Prepared by heating oxycomenie acid C₂HO₂(OH)₂ CO₂H with conc NH₂Aq at 160° (Reibstein, J pr. [2] 24, 290 g Ost, J pr [2] 27, 265) Small needles (contain-

ing aq) (from water). Does not form a hydro chloride Gives an azure pp with BaCl, and NH₃ Alcoholic potash gives, in alcoholic solutions, a blue floccalent pp, forming a colourless solution in water FeCl, gives an indigo blue colour AgNO, gives a white pp, soon turning Br forms bromo tri oxy pyridine carb oxylic acid, crystallising with 2aq Nitric acid added to the ethereal solution forms oxypyridoquinone carboxylic acid C,HNO,(OH) CO,H, crystallising in orange tables (containing 2aq)

References - Bromo , Chloro , and Bromo-

NITBO-, OXY PYRIDINE CARBOXYLIC ACID OXY PYAIDYL ETHYL FURFURANE

 $\mathtt{CH} \underset{\mathrm{CH \ N}}{\overset{\mathrm{CH \ CH}}{>}} \mathtt{C} \ \mathtt{CH_2 \ CH(OH)} \ \mathtt{C} \underset{\mathrm{CH \ CH}}{\overset{\mathrm{CH \ CH}}{>}} \mathtt{CH} \ \mathtt{[43°]}.$ Formed from (a) methyl-(164° at 20 mm) pyridine, furfuraldehyde, and some water at 150° (Klein, B 23, 2693) Greenish mass, v sol alcohol —B'H.PtCl, [162°] —B'HHg [c 150°] —B'HCdI, —B'C,H,N,O, [c 160°] Acetyl derivative Oil — [162°] —B'HHgCl,

 $(C_{11}H_{10}AcNO_2)_2H_*PtCl_s$ [165°] $-B'HHgCl_s$ [0 155°] Small needles

Bensoyl derivative C₁₁H₁₀BzNO₂ [49°]. -B'₂H₂PtCl_e [140°-145°] —B'HHgCl₁ OXY PYRIDYL-MALONIC ACID

C₅H₄N C(OH)(CO₂H)₂ Formed by oxidising plocarpine with KMnO₄ (Hardy a Calmels, Bl. [2] 48, 228) Syrup Yields pyridine (β) carb oxylic acid on further oxidation—BaA"—Ba A'' 3aq—Cu, A''(OH) aq—Ag, A'' pp

OXY-PYRIDYL-PHENYL-PROPIONIC ACID Hexahydride C,H10N CHPh CH(OH) CO,H. Formed from piperidine and sodium phenyl glycidate (Erlenmeyer, B 22, 1482)

α-OXY (β)-PYRIDYL PROPIONIC ACID C,H,N CH2 CH(OH) CO.H Formed by boiling pilocarpine with water for 12 hours (Hardy a Cal mels, Bl [2] 48, 227) Gummy mass — B'HCl —
B'₂PtCl₄ — B'AuCl₃ [154°] Prismatic needles
a Oxy-(a)-pyridyl propionic acid

 $C_5H_4N CH_2 CH(OH) CO_2H$ [125°] Formed by the action of hot dilute caustic soda on C₃H₄N CH₂CH(OH) CCl₃, the product of the union of chloral with (a) picoline (Einhorn, B 23, 219, A 265, 211) Prisms —Cu₂A'₂O needles — (HA'). H. PtCl_s [204°] — HA'HAuCl₄ [174°] Orange prisms — AgA' white needles -HA'HCl [86°] -HA'HBr

Benzoyl derivative [145°] Needles -

B'2H,PtCl, [179°] Yellow prisms

Methylether MeA'—MeA'HAuCl, [119°] Benzoyl derivative of the C₁H₄N CH₂CH(OBz) CO₂Me [c 41°] Yields B'₂H₂PtCl₆, [193°], crystallising in yellow needles β Oxy-(a) pyridyl propionic acid

C₅H₄N CP₂(OH) CH₂ CO₂H [86°] Formed by warming B bromo pyridyl propionic acid with NaOHAq (Einhorn, B 23, 221) White needles, We sol water — Cu.A',O blue crystals — B'HCl [147°] Prisms — B',H,PtCl [191°].

Benzoyl derivative [1855°] Prisms

Benzoyl derivative [1855°] Prisms Methylethyl MeA' Yields (MeA')₂H₂PtCl₆ [178 5°] and a benzoyl derivative [79°] crys-

tallising in prisms Ethylether EtA' Yields (EtA')2H2PtCl.

Di-oxy-pyridyl-propionic acid C,H,N CH(OH) CH(OH).CO,H [190°] Formed by oxidising pyridyl-acrylic acid with alkaline KMnO, (Einhorn, B. 23, 223). White crystals

Ethylether EtA' [96°] Tables Yields a benzoyl derivative [1220] crystallising in needles

DI-OXY-PYRIMIDINE v HYDROQUINOME TETRACARBOXYLIC ACID

OXY-PYRONE DICARBOXYLIC Ethyl derivative of the ethyl ether

 $CH \leqslant_{C(CO_2Et)-CO}^{C(CO_2Et)} > 0$ Anhydride of tri-

ethyl propylene-tetracarboxylate [94°] Formed by distilling di carboxy-glutaconic ether at 210° under 15 mm pressure (Guthzeit a Dressel, B 22, 1415) Needles, insol water and alcohol.

22, 1415) Needles, insor national acid Converted by HClAq into glutaconic acid OXY-PYROTARTABIC ACID C₃H₃O₃ t.6 CH, C(OH)(CO₂H) CH₂ CO₂H Formed by the action of boiling dilute HCl upon CH, C(OH)(CN) CH, CO,Et, which is got by heating acetoacetic ether for three days with dry HCy at 100° (Morris, C J 37, 7, cf Demarçay, Bl [2, 27, 120) Made also by oxidation of isovaleric acid by long boiling with dilute HNO₃ (Bredt, B 14, 1782, 15, 2318) quescent, star like groups of needles, sol water, alcohol, and ether On dry distillation it splits up into water and citraconic anhydride — BaA" 2aq Not decomposed by boiling with water — CaA" 1½aq — Ag, A' ½aq needles

Oxy-pyrotartaric acid CH₃ CH(CO₂H) CH(OH) CO₂H Crtramalic acid [119] Formed by the action of zinc on a dilute solution of chloro citramalic acid (which melts at 139° according to Melikoff, A 253, 88), HCl is added towards the end of the reaction (Carius, A 129, 160, Morawski, Sitz W 76 [2] 670, J pr [2] 10, 69) Large hygroscopic crystals, yielding citraconic anhydride and water on distillation — Salts K.A" xaq — BaH₂A" 2aq — MgA" — CaA" 2aq — CaA" 1}aq — CaH₂A" 2āq — ZnA" 2aq — PbA" 3½aq — Ag.A"

Oxy pyrotartaric acid CH (OH) CH(CO.H) CH CO2H Itamalic acid. Formed from itaconic acid by successive treatment with HBr and hot water Formed also by boiling ita chloro pyrotartaric acid with aqueous Na CO₃ (Swarts, Bull Acad Belg [2] 24, 25, Bl [2] 9, 317, Fittig, A 188, 76, Morris, C J. 37, 14) The free acid, liberated from its Ca changes on evaporation, even at 15°, into its lactone [58°] —Na.A" —(NH.)HA" —CaA"aq —CaA"3aq —PbA" —CuA" —Cu,A"30 —AgA —EtA' oil salt by oxalic acid, or from its Ag salt by H2S,

Lactone CH(CO₂H) < CH₂CO CH₂CO Paraconic. acid [58°] Formed as above, and also by boiling ita bromo pyrotartario acid (1 pt) with Crystalline. water (10 pts) (Beer, A 216, 90) Yields citraconic anhydride on distillation With bases it yields salts of itamalic acid -NaC, H,O, -CaA', 3aq Small needles Yields calcium itamalate on boiling with CaCO, -AgA'

Chloro-itamalic acid C,H,ClO, Made by passing chlorine into a solution of sodium itaconate Crystals, v e sol water

Oxypyrotartaric acid [c 135°] described by Maxwell Simpson (Pr 13, 44) as got from glycerin dichlorhydrin by successive treatment with KCy and KOH, is probably 8 oxy glutarie acid. It yields Ag.A" and Et.A" (298°) An isomeric or identical acid, made by fusing sulpho-pyrotartaric acid with potash, yields Ag₂A" aq (Wieland, A 157, 41) A liquid isomeride, got by potash fusion from bromo-eyano-butyric acid, yields Ag.A"

Di-oxy pyrotartaric acid C.H.O. Citratar-taric acid Formed by the action of boiling baryta water on chloro citramalic acid prepared from barium citraconate and HOCl (Carius, A 129, 159) and by heating oxycitraconates with water at 120° (Morawski, J pr [2] 11, 432) Amorphous, deliquescent mass —Pb,A" aq

Isomeride v Itatartaric acid

DI-OXY-DI-PYRRYL-BUTANE C12H6N2O2 C₅H₄N CMe(OH) CMe(OH) C₅H₄N [120°] Formed from pyrryl methyl ketone, water, and sodium amalgam (Dennstedt a Zimmermann, B 19, 2204) Monoclinic prisms (containing 2aq) Melts at 98° when hydrated V e sol alcohol

OXY PYRUVIC ACID C₃H₄O₄ i e I₂(OH) CO CO₂H Formed by dissolving CH₂(OH) CO CO₂H 'nıtro cellulose' (collodion) in dilute NaOHAq and allowing the solution to stand at 20° (Will, B 24, 405) Amorphous, v sol water, but ppd Reduces Fehling's solution and by alcohol ammoniacal AgNO. Its solutions, and those of its salts, are slightly lævogyrate Phenyl hydrazine forms the compound $C_{15}H_{14}N_4O_7$ or $(N_2HPh)CHC(N_2HPh)CO_2H, [205°], whence$ NaA' [231°], KA' [233°], NH,A' [200°], CaA', and EtA' [149°]

Salts — CaA', 8aq — SrA', 4aq — CdA', 4aq OXY QUINALDINE v OXY METHYL QUIN-

OXY QUINAZOLINE Dihydride

C₆H₄<CH₂NH NH CO 'Phenuldihudroacimiazine' [160°] Formed from oxy tolyl ures and HCl (Soderbaum a Widman, B 22, 1669) insol cold conc KOHAq —B'HCl — B'₂H₂PtCl₆ 2aq [205°] —B'HAuCl

Oxy-quinezoline $C_{\epsilon}H_{\epsilon} < C(OH) \stackrel{N}{N} = CH$ [212°] Made by heating formyl o amido benzamide [123°] for two hours at 180° (Knape, J pr [2] 43, 214) Thin needles —B'2H2PtCle aq [above

250°

Methyl derivative [71°]. Di oxy quinazoline

 $C_6H_4 < N = COH$ 'Uramido benzoyl' [above Formed by passing cyanogen into an alcoholic solution of o amido benzoic acid and boiling the product with HClAq Formed also by fusing oamido benzoic acid or oamido benzamide with urea, and by heating the product of the action of ClCO₂Et on o amidobenzamide (Griess, B 2, 415, 11, 1985, Abt, J pr [2] 39, 140) Needles, sl sol hot water With POl, it yields di chloro quinazoline [115°]

-C₈H₄NaN₂O₂EtOH needles Di-methyl derivative C₈H₄(OMe)₂N₂. Made from di chloro quinazoline and NaOMe Needles, v e sol alcohol

OXY p.QUINAZOLYL-BENZOIC ACID

C.H. CON C.H. CO.H. Made by oxidising p. tolyl quinazoline dihydride with KMnO, (Paal a. Busch, B 22, 2699) Small needles -

OXY-QUINHYDRONE C₁₂H₁₀O. Formed from oxyhydroquinone and HNO₂ (Barth a. Schreder, M 5, 595) Dark greyish-blue crystals. B' (H.SO.) 11aq — B'HCl aq. prisms, v e sol.

1)-OXY-QUINOLINE C.H. CO CH [235°] Made by heating phenyl-\$\beta\$ amido acrylic acid at 200° or examilic acid at 170° (Reissert, B 20, 3109, B 21, 1376) Lyng needles (from Yields quinoline when distilled with alcohol) zınc dust

Acetyl derivative [228°] Needles Phenyl hydrazide C₁₈H₁₈N₁ [168°] (Py 2)-Oxy-quinoline This is probably the constitution of cynurine v infra

 $C^{e}H^{4} < \stackrel{N=0}{\sim} OH$ 3) Oxy-quinoline

Carbostyril [199°] N Formation —1 By reducing o nitro cinnamic acid (Chiozza, A 83, 118, Tiemann, B 13, 2070, Friedlander, B 14, 1916) -2 By heating oamido cinnamic acid with HClAq (T) or dilute H_2SO_4 (Feer a Königs, B 18, 2395) -3 By re ducing tri chloro-oxy quinoline with HI -4 By heating (Py 3) chloro quinoline with water at 120° (Friedlander a Ostermaier, B 15, 335) -5By the action of aqueous HOCl upon quinoline (Erlenmeyer a Rosenhek, B 18, 3295) -6 By heating quinoline on the water bath with a conc solution of bleaching powder (E a R, B 19, 489, Roos, B 21, 619)

Properties - Long thin feathery crystals (containing aq) (from water) or thick anhydrous prisms (from alcohol), v sl sol cold water, insol NH,Aq

Salts — Ba(C₂H₂NO). plates — AgA' pp

Methyl ether MeA' (247°) Oil

Ethyl ether EtA' (256°) Formed from

(Py 3) chloro quinoline and KOEt Formed
also by heating o amido cinnamic ether with
alcohol and ZnCl₂ at 90° (Friedlander a Wein berg, B 15, 1424, 2103) and by ethylation of carbostyril Pungent oil, solidifying below 0° Yields a dihydride [199°] when reduced by sodium amalgam

Phenyl ether [69°] Plates Dihydride v AMIDO PHENYL PROPIONIO

CH C(OH) C CH CH CH CH — C N CH (B 1)-Oxy-quinoline [224°] Formed by potash fushion from quinoline (Py 1) sulphonic acid (Riemerschmied, B 16, 721, Lellmann, B 20, 2174) Formed also from (Py 1)-amido-quinoline by the diazo reaction (Skraup, M 5, 533) Silky needles or plates, sol alcohol and aqueous Na2CO3, v sl sol water—Salts BHCl yellow needles— B'2H2PtCl44aq orange tables

Tetrahydride C.H. (OH) CH2 CH2 CH2

[117°] Made by reducing with tin and HCl Needles, sol water, alcohol, and ether Yields a nitrosamine crystallising in tables, sol alcohol

C(OH) CH C CH CH CH CH — C—N CH (B 2) Oxy-quinoline [193°] (above 360°) Formed by heating a mixture of p amido-phenol, p nitro phenol, glycerin, and H₂SO₄ (Skraup, B 15, 893, M 3, 545) Formed also by heating its carboxylic acids (Weidel, M 2, 575, Skraup, M 4, 696) and by potash-fushion from its sulphonic acid (Fischer, B 17, 440) Small prisms (from alcohol) Not coloured by ferric chloride solution B'sH.PtOl, 2aq [236°] — B'sCu(OAc). water — B'MeI aq Crystalline (Claus a Howitz, J pr [2] 42, 282, 43, 520) — B'MeCl [c 272°] -B'₂Me₂PtCl₄ -B'Me₂SO₄ 5aq -B'MeOH [c 2000] -B'EtBr [c 2420] -B'C,H,Cl 1½aq

[287°] —(B'O,H,C1),PtCl,

Methyl ethir MeA' p Quinanisole (305°)

S G 2 1 665 Got by methylation, and also from pranisidine, nitro anisole, glycerin, and H2SO4 (Skraup, M 6, 762) Oil Solutions of its salts show blue fluorescence Gives a green colour with chlorine water and ammonia -B'HCl 2aq — B'₂H₂PtCl₆ 4aq — B'H₂SO₄ — B'₂H₂SO₄ — B'₂H₂Cr₂O₇ — B'MeI [235°] Prisms — Picrate [204°]

tyl derivative C,H6(OAc)N [38°] (298°) C1 ystals -B'2H2PtCl6 Prisms

Benzoyl derivative [231°] Needles Tetrahydride of the methyl ether C₉H₁₀(OMe)N Thallin [43°] (283°) at 735 mm Got by reducing the methyl ether with tin and conc HClAq Prisms FeCl, gives a golden colour, changing to emerald green -Chlorine water gives a green colour turned yellow by ammonia —B'HCl —B'₂H₂SO₄ 2aq —B'HI [155°] -B'C,H,O, four sided prisms S 10 at 15° -Picrate [162°] Acetyl derivative C,H,Ac(OMe)N [47°]

[c 238°] Formed by heating m-nitro phenol with m amido phenol, glycerin, and H₂SO₄ (Skraup, B 15, 893, M 3, 559) Formed also by potash fusion from quinoline (B 3) sulphonic acid (Fischer, B 15, 1979) Silky needles, sol alcohol, not volatile with steam Its solutions show green fluorescence FeCl, gives a brownsh red colour -B'2H2PtCl62aq -B'HCl12aq prisms —B'Cu(OAc)2 —Picrate

sms —B'Cu(OAc), —Prorate [244]
Benzoyl derivative [86°] Prisms
Methyl ether C₁₀H₂NO (275° at 720 mm) Oil, volatile with steam

ÇH CH — C CH CH (B 4) Oxy quinoline CH C(OH) C-N CH

[75°] (267° cor)

Formation -1 By distilling its carboxylic acid (Weidel a Cobenzl, M 1, 862) -2 By soda fusion from its sulphonic acid (Bedall a Fischer, B 14, 443, 1366) -3 By heating o amido phenol with o nitro phenol, glycerin, and H2SO4

(Skraup, B 15, 893, M 3, 536)

Properties — Prisms, sl sol water May be distilled with steam FeCl, gives a green colour Gives quinolinic acid on oxidation with KMnO. (Fischer a Renouf, B 17, 756) Chlorine in HOAc forms mono, di-, and tri, chloro derivatives (Zincke a Hebebrand, A 264 Ethylene chlorhydrin forms crystalline (C₁₁H₁₂NO₂Cl)₂PtCl₄) ClCO₂Et forms B'(C₂H₄OH)Cl, whence (Wurtz, C R 96, 1269) (Lippmann, M 8, 439)

mann (M 10, 667), MeI in MeOH at 100° forms (C,H,(OMe)N)(C,H,(OH)NMeI)HI 2aq, C₂₀H₁₉ClN₂O₂HCl 5aq and C₂₀H₂₀Cl₂N₂O₂PtCl₄2aq

These bodies may perhaps be more simply formulated, as below Chloroform and Na yield CH(C₂H₄(OH)N). (Lippmann, B 19, 2471)
Salts -B'HClaq -B'₂H₂PtOl₂ 2aq golden needles -B'H₂SO₄ 2aq -B'C₂H₂N₃O, [204°].
Cu(C₂H₂NO)₂ canary-yellow pp -B'MeI aq [c 170°] -B'MeCl 2aq [c 260°] -B'₄Me₂PtCl₂ 2aq

Acetyl derivative CoH. (OAc)N (280°). Oil —B',H,PtCl, 2aq yellow plates Benzoyl derivative [120°]

Crystals Methyl ether C.H. (OMe)N (268°) Got by methylation, and also from o amido anisole by Skraup's reaction Oil -B'2H2PtCl, 2aq - $B'HCl - B'C_{\epsilon}H_{\bullet}N_{\bullet}O_{\tau}$ yellow needles or plates Leaflets (Claus a Howitz, -B'MeI aq [160°] J pr [2] 42, 229

Ethyl ether C.H. (OEt)N (286°) at 718 mm Needles (Fischer a Renouf, B 17, 759) —

Picrate [181°] Yellow needles

Tetrahydride C.H.(OH) C.H.,N [122°]
Made by reducing (B 4)-oxy-quinoline with
SnCl. (Fischer, B 14, 1368, 14, 2571, 16, 713, 17, 759) Needles or prisms, sol hot water Yields a nitrosamine [68°] The methyl ether C₉H₁₀(OMe)N is oily and yields a crystalline hydrochloride and a nitrosamine [80°] ethyl ether is also liquid (275°) at 715 mm, and forms a crystalline nitrosamine [113°] and

an oily acetyl derivative (307°) Oxy quinoline C₂H,NO Cynurine [201°] above 300°) S 477 at 15° Probably (Py 1)or (Py 2) oxy quinoline Formed by heating its carboxylic acid (cynurenic acid) (Schmiedeberg a Schultzen, A 164, 158, Kretschy, M 2, 68) Formed also by oxidising cinchonine or cinchonic acid (Skraup, M 9, 821, 10, 729) Monoclinic prisms (containing 3aq), m sol hot water Melts at 52° when hydrated Tastes bitter KMnO, oxidises it to cynuric acid ICl gives a brownish pp [275°] (Dittmar, B 18, 1618) Distillation with zinc dust forms quinoline Ac₂O on heating forms an indigo blue dye Yields a tetrahydride —B',HCl 2aq monoclinic prisms
—B'HClaq —B',2H,2PtCl,2aq orange needles
(Py 2, 3) Di oxy-quinoline

 $C_eH < CHCOH$ **β-Oxy-carbostyril** 300° Prepared by heating (Py 2, 3) chloro oxy quinoline (β chloro carbostyril) with fused KOH at 200° (Friedlander a Weinberg, B 15, 2681) Fine colourless needles Maybe sublimed Is a very weak base but a strong acid, it dissolves in concentrated HCl, but is reprecipitated on dilution By PCl, it is converted into the di chloro-quinoline [104°] -A'Ag crystalline

Dr-oxy-quinoline $C_0H_1 < N = COH$ [above

320°

Formation -1 By the action of conc H.SO. on o amido phenyl propiolic acid (Baeyer a Bloem, B 15, 2151) -2 By potash fusion from (Py 1, 3) bromo oxy quinoline (Friedlander a Weinberg, B 15, 2683) -3 By reducing o nitro benzoyl malonic ether with tin and HCl (Bischoff, B 22, 387, A 251, 377) -4 By boiling its carboxylic acid with cone HClAq (B)

Properties - Needles, sol Na₂CO₃ and in a mixture of alcohol and HClAq, insol ordinary menstrua Its ammoniacal solution turns blue in air PCl, yields di-chloro-quinoline [67°]
Salt—C,H,AgNO, needles

Ethyl ether C.H. COH CH COEt [228]. Formed by reducing o nitro benzoyl malonic ether with tin and HCl (B) Slender needles

Dihydride C.H. CH(OH) CH. C(OH) Formed by reducing o-mitro-\$-oxy phenyl propionic soid with FeSO, and NH, (Einhorn, B 17, 2011) Needles (containing 2aq) melting at 96° when hydrated Readily splits off water, yielding carbostyril

(B 14)-Di-oxy-quinoline

CH C(OH) C CH CH CH C(OH) C—N CH Quinoline-hydroquinone Formed by reduction of quinoline quinone by SO₂ (Fischer a Renouf, B 17, 1645) Thin needles V sol water, al sol cold benzene Decomposes about 220°

Salts -The hydrochloride forms orange needles, the sulphate forms sparingly soluble

orange-yellow needles

Di oxy-quinoline C₉H₅(OH)₂N a Oxyquinophenol [189°] Got as a bye product by fusing (Py 1, 3)-bromo oxy-quinoline with potash (Friedlander a Weinberg, B 15, 2684) Concentric needles y col centric needles, v sol most solvents PCl, yields chloro-oxy quinoline [180°] -AgA' crystalline

D1-oxy-quinoline C9H5(OH)2N Oxycarbostyril [191°] Got as a by product in the pre paration of carbostyril from o nitro cinnamic ether and alcoholic ammonium sulphide (Friedlander a Ostermeyer, B 14, 1916) Needles or plates, sl sol hot water May be sublimed Coloured red by HNO, Reduced by tin and HCl to carbostyril Alkaline KMnO, oxidises it to o nitro-benzoic acid —BaA'₂ needles Ethyl ether C₉H₈EtNO [73°]

Ethyl ether C. H. EtNO [73°] Prisms, insol water May be distilled —B'HCl hygro-

scopic crystals -B'2H2PtCl8 Crystals

Di oxy-quinoline C_aH_s(OH)₂N [130°-136°] Formed from quinoline (a) di sulphonic acid by fusion with potash at 260° (La Coste a Valeur, B 19, 997, 20, 1821) Needles (from benzene), v sol ether Oxidises in air —B'HCl aq [2569] B'₂H₂PtCl₆2aq yellow pp —B'C₆H₃N₃O₇ [227°-237°] Yellow needles, v sol warm water

Mono-acetyl derivative C.H.AcNO. [117°] White needles (from warm water)

Di-bensyl derivative C,H,Bz,NO,

[130°-134°] Needles, v sol alcohol

Mono methyl ether CoH, (OH) (OMe) N Formed by methylation Liquid, sol hot water—B'HCl aq [255°-259°] Yellow needles—B'2H_PtCl₆ 2aq needles.—B'C₆H₅N₅O, [221°-226°] Needles si sol cold water [221°-

De-methyl ether CoH, (OMe)2N Liquid, sl sol hot water —B'HCl aq [262°-266°] -B' H.Pt.Cl, 4aq monoclinic — B C,H,N,O, [104°] —B'MeI [212°] Monoclinic tables — (C,H,Me,NO,)(C,H,NO,)MeI [207°] Crimson needles — (C,H,Me,NO,),C,H,NO,MeI [170°] Lemon yellow needles

Di-oxy-quinoline C₂H₅(OH)₂N [68°] Made by potash fusion from quinoline (β) disulphonic acid (La Coste a Valeur, B 20, 3200) Needles

Di-methyl Di-oxy-quinoline ether C.H. (OMe)2N Got from veratric acid (derived from eugenol) by nitration and reduction, the resulting amido veratric acid being heated with ntro benzene, glycerin, and H₂SO₄ (Gold schmiedt, M 8, 342) Oil — Salts B'HClaq —B'₂H₂PtCl₃aq —B'C₆H₃N₄O, [257°] —B'₂H₂Cr₂O, yellow crystalline pp Di-oxy quinoline C₃H₄(OH)₂N. Formed from

quinoline (B 1) sulphonic acid by potash fusion (Lellmann, B'20, 2174) Needles, not melted at 320°—B'₂H₂PtCl₄ needles

Di-oxy quinoline Acetyl derivative of the tetrahydride C,H,(OH)(OAc)N Formed by reducing (Py 2)-nitroso (Py 3) oxy-carbo styril with zinc-dust and HOAc (Baeyer a Ho molka, B 16, 2217) Colour ss needles, sl sol water, sol HOAc Forms a hiue solution with

(B 2, Py 3) D1-oxy-quinoline derivative C(OMe) CH C CH CH CH CH ——C N=C OH Methal [219°] Got by the action of ammonia and FeSO on $[2\ 5\ 1]C_6H_3(NO_2)(OMe)\ CH(OH)\ CH_2\ CO_2H$ (Eichengrun a Einhorn, A 262, 179) v sol alcohol

Tri oxy quinoline methyl derivative Dihydride of the

 $C_eH_3(OMe)$ $< N = CH(OH) CH_2 CH$ [177°] Got at the same time as the preceding body Needles

(Py 1,2,3)-Tri oxy-quinoline C₆H₄<N=COH Formed Formed by reduction of (Py 2) nitroso (Py 3) oxy carbostyril with SnCl, (B a H) Needles, v sol alcohol, v sl sol water Yields quinisatic acid C₆H₄(NH₂) CO CO CO₅H on oxidation with FeCl,

References -DI BROMO, CHLORO, and IODO,

OXY QUINOLINE

DI OXY ISOQUINOLINE Di methyl ether CoH5(OMe)2N Formed, together with vera tric acid, by fusing papaveraldine with potash Formed also by heating its carboxylic acid, which is a product of the oxidation of papaverine (Goldschmiedt, M 7, 494, 8, 510, 9, 344) Yields hemipic and cinchomeronic acids on oxidation —B'HCl 3aq —B'C₈H₃N₃O₇ B'12H.Cr2O,

(Py = 3) OXY-QUINOLINE (P1)-CARB OXÝLĬC AĆID

 $C_{10}H_7NO_3$ re $C_6H_4 < N = COH$ Oxycinchonic acid Carbostyril carboxylic acid Mol w 189 [above 310°] Got by fusing cin chonic acid with potash (Konigs, B 12, 99, 16, 2152) Needles, sl sol water May be sub Its Ag salt yields carbostyril on distil lation -CuA'2 -AgA' white pp Ethyl ether EtA' [207°]

Needles Ethyl derivative CaH3(OEt)(CO.H)N [146°] Made from chloro quinoline carboxylic acid and NaOEt Needles Changes to the isomeric ethyl ether when heated above 146° -

C₂H₃(OEt)(CO₂Et)N [86°] Needles

(Py 3) Oxy-quinoline (Py 2) carboxylic acid C'H' CH C CO'H [above 320°] Made by heating o amido benzoic aldehyde with malonic acid at 120° (Friedlander a Gohring, B 17-459), and also by reducing o nitro tenzylidene malonic acid (Stuart, C J. 53, 143) Small needles, v sl sol water, m sol HOAc PCl. yields chloro quinoline carboxylic acid [200°], whence KOEt forms the ethyl derivative

C₃H₄(OEt)(CO₂H)N [138°] — BaA'₂ — AgA'; gelatinous pp — Ag₂C₁H₄NO₄ needles
(B 4)-Oxy quinoline (Py 1) carboxylic acid
C₁₀H₄NO₅ * 6 CH CH — C C(CO₂H) CH
CH C(OH) C — N CH
CHCOMPARA CAST (CO²CO) [256°] Formed by fus-Oxycinchonic acid` ing (a)-sulpho cinchonic acid with potash

(Weidel a Cobenzi, M 1, 855) Minute prisms

(containing aq), sl sol hot water, m sol hot alcohol Gives a green colour with FeCl, Yields (B 4) oxy quinoline on distillation, and pyridine
(a) tri carboxylic acid on oxidation—BaA'₂—
BaC₁₀H₃NO₃aq—\gHA'₂aq—AgA'—HA'HCl
moncolinic needl's—B'₂H₂PtCl₆2aq needles

(B 2) Oxy quinoline carboxylic acid $C_{10}H,NO_2$ (3) Oxy cinchonic acid [c 320°], Made by potash fusion from (3) sulpho cinchonic acid (Weidel, M 2, 571) Tables (containing aq), sl sol water Yields (B 2) oxy quinoline on distillation, and a pyridine tricarboxylic acid on oxidation -BaA'2 -HA'HClaq needles -(H ') H,PtCl 2aq monoclinic tables, decom posed by water

 $(B\ 3)\ { t Oxy}\ { t quinoline}\ ({ t Py}\ 1?)\ { t carboxylic}\ { t acid}$ C10H,NOs Xanthoquinic acid [above 300°] Possibly identical with the preceding acid by heating quinic acid with cone HClAq at 225° (Skraup, M 2,601, 4,695) Yellow grains Yields (B 2) oxy quinoline on distillation — Salts BaA', 6aq - CaA', 10aq - CuA', aq AgA' 2aq — HA'HCl 2aq — H.A'₂H,PtCl₆ baq —

HA' H SO 3aq golden prisms

Wethyl derivative CoH, (OMe) (CO,H)N Quininic acid [280°] Made by oxidising quinine or cinchonine with chronic acid (Skraup, M 2, Thin yellowish prisms, sl sol hot water and hot alcohol, nearly insol ether Its alco holic solution shows blue fluorescence, destroyed by H₂SO₄ KMnO₄ oxidises it to pyridine tri carboxylic acid — Salts BaA' 4aq — CaA', 2aq — CuA' 1¹aq — AgA' pulverulent pp HA'HCl 2aq tuclinic tables — H,A',2H PtCl, 4aq yellow crystals

(B 4) Oxy quinoline carboxylic acid

C10H,NO [280°] Made by boiling o oxy quinoline with CCl4, water, KOH and alcohol (Inppmann a Fleissner, B 19, 2467, M 8, 318) Minute prisms, v sl sol hot water Yields (B 4) oxy quinoline on distillation, and pyridine dicarboxylic (quinolinic) acid [235°] on oxidation FcCl, gives a green colour Yields a di bromo denvative [193°] —BaC₁₀H₃NO₃ aq needles -AgHA'₂ (dried at 105°) Minute needles

AgHA'₂ (dried at 105°) Minute needles

Tetrahydride C₁₀H₁₁NO₃ [265°] Got by
reduction with tin and HCl Prisms, sl sol water, almost insol ether Reduces AgNO, in the cold Gives a red colour with FeCl, yields C10H10EtNO3HI, whence C10H10EtNO3 [220°] may be got Nitrous acid for amine [195°] — (C₁₀H₁₁NO₃)HCl aq B' H₂SO₄ 3aq — B'HOAc pp Nitrous acid forms a nitrosneedles

 $(B\ 4)\ \mathbf{0xy}\ \mathbf{quinoline}\ \mathbf{carboxylic}\ \mathbf{acid}$

 $C_{10}\dot{H}_1NO_3$ aq [250°] Got from o oxy quinoline dithiocarboxylic acid $C_0H_3(OH)(CS\dot{H})N$ by warming with lead acetate and KOHAq (Lipp mann a Fleissner, M 9, 300) Silky needles, Silky needles, sol water Coloured red by FeCl₃ Yields o oxy quinoline on distillation —KA'—BaA', (dried at 130°) - AgA' - Hg.A',Cl₂ - H,A',H,PtCl₄ 4aq - HA'HCl 2 aq trimetric crystals [222°] Crys

Tetrahydride C₁₀H₁₁NO₃ [222°] Crystalline powder —B'HCl needles, v sol water

(B 4) Oxy quinoline carboxylic acid C,H, (OH)(CO,H)N Formed by heating sodium o-oxy quinoline with liquid CO, in a closed vessel at 150° (Schmitt a Engelmann, B 20, 1217, 2690) Small yellow prisms (containing aq), m sol hot water and hot alcohol. Coloured red Vol III

by FeCl₃ At 150° it splits up into CO2 and ooxy quinoline Yields C10HeBrNO, [2350

Salts -B'HCl needles - B'HNO, -NH,A' aq -BaA', 2aq needles, sl sol water -BaC₁₀H₅NO₅ amorphous, v sl sol water — AgA' amorphous powder

Phenylether PhA' [226°] Made by heating the acid with phenol and POCl, at 170°. Prisms

Tetrahydride C9H9(OH)(COH)N Colour less prisms -B'HCl prisms MeI and MeOH

at 100° form C₉H₈Me(OH)(CO₂H)N [211°], which crystallises with 2aq

(B 2) Oxy quinoline carboxylic acid $C_0H_3(OH)(COH)N$ [204°] Formed by boiling p oxy quinoline with NaOH, CCl., water, and alcohol (Lippmann a Fleissner, M 8, 324) Made also by heating potassium (not sodium) p oxy quinoline with liquid CO at 170° (Schmitt a Altschul, B 20, 2695) Minute prisms, v sl sol hot water and alcohol Splits up at 200° into CO, and p oxy quinoline Yields quinolinio acid on oxidation - HA'HCl - HA'HNO, needles — H A'₂H₂PtCl₆2aq — NH₄A'₂aq needles, v sol hot water — BaA'₂2aq CaA', 6aq —PbC, 6A, NO, aq —CaA', 6aq needles - AgA'

Oxy quinoline carboxylic acid C₁₀H,NO₂. Cymurenic acid [258°] S 9 at 100° Occurs in the urine of dogs after a fat diet (Liebig, A 86, 125, 108, 354 Voit a Richter, J 1865, 676, Schmiedebeig a Schultzen, A 154, 155, Hof-meister, H 5, 70), or a diet of flesh only (Kretschy, M 2, 57, 5, 16) Prisms (con-taining aq) insol cold water Decomposed by heat into CO and oxy quinoline Yields quin oline on distillation with zinc dust Evapora tion with KClO, and HCl leaves a residue which is turned emerald green by ammonia (Jaffé, H. (Brieger, H 4, 92) — NH, 4'—KA'2aq — BaA' 4¹aq — BaA' 3aq —CaA' 2aq — CuA'2aq — AgA'aq thick white pp

 $(Py \ 3)$ Oxy quinoline $(B \ 3)$ carboxylic acid. Dihydride CH CH CH C CH CH CH CO. _сснсн, [above Prepared by the reduction [3 1 4] C, H, (NO,) (CO H) CH CH, CO, H with ammonia and FeSO, (Widman, B 22, 2274) Yellow plates (from water), v sl sol alcohol Yields a methyl ether MeA' [192°] crystallising in tables

Di-oxy-quinoline carboxylic acid

derivative of the ethyl ether $C_eH_t < N \xrightarrow{C \text{ OEt}} [107^\circ]$ Got by the action of zinc, alcohol, and gaseous HCl on onitro benzoyl malonic ether (Bischoff, B 22, 386) Small needles

o) Small needles Coloured violet by FeCl.
Tetra oxy quinoline carboxylic acid Lact one of the di methyl derivative of the dihydride C12H11NO, te Ç0 Ŏ-

C₆H(OMe), CH CH₂ NH CO [c 256°] Prepared by

the reduction of onitro meconin acetic acid

CO O $C_0H(NO_2)(OMe)_2$ with tin and CH CH, CO,H

HCl (Liebermann & Kleemann, B 19, 2296) Colourless needles (from water), v sol alcohol Boiling baryta water yields Ba(C₁₂H₁₂NO₆)₂ 6aq. Hi and HOAe at 120° form C₁₆H,NO₄ [220°], a srystalline solid PCl₃ yields C₁₂H₁₆CINO₄ [218°]. DI -OXY - ISOQUINOLINE CARBOXYLIC

ACID C₁₈H₁₁NO₄ [221°] Formed by heating its di-methyl derivative with HIAq Yellow powder FeCl, gives a violet colour When heated it yields a compound [230°] which gives FeCl, gives a violet colour isoquinoline on distillation with zinc dust

Di-methyl derivative C,H,(OMe),(CO H)N [205°] Got by oxidation of papaverine (Goldschmiedt, M 6, 964, 8, 519, Yellow needles (containing 2aq) -HA'HĆl 2aq needles

OXY-QUINOLINE SULPHONIC ACID

C₂H₃(OH)(SO₂H)N Formed by fusing quinoline (a)-disulphonic acid with potash (La Coste a Valeur, B 19, 997, 20, 100) Pale-yellow plates (containing aq), sl sol water — KA'aq prisms, v e sol water — BaA'₂ 3aq. — CaA'₂6aq — CuA'₂4aq green needles — CaC₂H₂NSO₄13aq — CuA', 4aq green needles — CaC, H, NSO, 1½aq —
BaC, H, NSO, 3aq yellow needles, sl sol water
Oxy-quinoline sulphonic acid
C, H, (OH)(SO, H)N [270°-275°]
Formed by

Formed by potash-fusion from quinoline (3) disulphonic acid (La Coste a Valeur, B 19, 998, 20, 3200) Yellow plates (containing aq), v sol hot water,

insol ether.

(B 3)-Oxy-quinoline sulphonic acid

C₂H₃(OH)(SO₂H)N [c 270°] Made from moxy-quinoline and fuming H₂SO₄ (Riemerschmied, B 16, 724) Yellow plates (containing aq), sl sol cold water

(Py 3) - Oxy - quinoline sulphonic acid Methyl derivative C.H. (OMe) NSO.H Formed from the methyl derivative of carbostyril and fuming H_2SO_4 (Feer a Königs, B 18, 2395) Needles, sol hot water -AgA' needles

(B 4)-0xy-quinoline (B 1)-sulphonic acid C_pH₃(0H)(SO₃H)N [270°] Formed by sulphonating o oxy quinoline by H₂SO₄ in the cold (Claus a Posselt, J pr [2] 41, 36) Needles (containing aq) FeCl₂ gives a green colour Salts — Na⁴Ca Na CH NGO Charles

Salts - NaA'aq - Na₂C₂H₃NSO₄ 2aq KA' aq - K₂C₂H₅NSO₄ Saq - BaA', aq. - A'_2 aq small needles, sl sol water $(B \ 4)$ -Oxy-quinoline sulphonic acid

 $C_vH_3(OH)(SO_vH)N$ Formed by heating o oxyquinoline with H_2SO_4 at 180° (Lippmann a Fleissner, M 10, 800) Crystals (containing 1 aq) Coloured green by FeCl, -KA' -BaA'. -AgA'

(B 2)-0xy-quinoline sulphonic acid C.H. (OH) (SO.H)N Made by sulphonating p oxy quinoline with fuming H₂SO₄ in the cold or at 100° (Claus a Posselt, J pr [2] 41, 159)
Yellow needles (containing ½aq), v sl sol cold water Decomposes at 270°—NaA' aq—KA' aq
Oxy-quinoline sulphonic acid C₁₀H,NSO₄

Formed by heating o-amido phenyl propiolic acid with H,SO, at 210° (Baeyer a Bloem, B 15,

2152) M sol cold water

(B 4) Oxy-quinoline disulphonic acid C,H,(OH)(SO,H)2N Made by heating o oxyquinoline with H₂SO₄ and P₂O₅ at 200° (L a F) Hygroscopic mass, decomposing at 200° FeCl₂ gives a green colour —KHA" —K₂C₂H₄NSO₇—

PaA" Saq —Cu, (C.H.NSO,), 10aq green pp OXY QUINOLINE DITHIOCARBOXYLIC ACID C.H. (OH)N CS.H [180°] Made by heating o-oxy-quinoline with potassium xanthate and alcohol at 100° (Lippmann a. Fleissner, M. 9.

296) Small red crystals, nearly insol water. FeCl. colours its aqueous solution brown. KMnO, yields quinolinic acid [281°] -NH,A'. Tables, al sol water

(a)-ONY (a)-DIQUINOLYL († , † , † , † , † .0 [208°] Made by fusing di-(Py 3) qu nolyl sulphonic acid with potash (Weidel, M 1, 312) Monoclinic needles (from xylene), insol water, sl soli hot alcohol -KA' aq -PbA', (dried at 100°).

Acetyl derivative [157°] Needles Oxy-(Py 3, B 1)-diquinolyl [187°] Got by fusing (Py 3, B 1) diquinolyl sulphonic acid with potash (Weidel, M 8, 144) Crystalline powder (from alcohol), v e sol alcohol

(B 2) Oxy-(Py 1, B 1 or 8) diquallyl Methylether C₁₀H₁₄N₂O ie

C₆H₅(OMe) $< \frac{C}{N} \stackrel{C}{CH} \stackrel{C}{CH} > C_6H_5 \stackrel{C}{CH} \stackrel{C}{CH} \stackrel{C}{CH}$ Two isomerides of this formula are formed together by heating m amido (Py 1) phenyl (B 2) methoxy quinoline with o nitro phenol, glycerin, and

H₂SO₄ (Miller a Kinkelin, B 20, 1924)
(a) Isomeride [151°] Thin monoclinic tables, sol alcohol and ether Solutions of its salts exhibit blue fluorescence -B"H2Cl, 2aq B"HCl — B"H-PtCl₂ 2aq — B"₂H₂PtCl₃ long needles —B"MeI yellow crystalline powder (β)-Isomeride [120°] Plates or flat mono-

clinic prisms Its alcoholic and ethereal solutions show blue fluorescence -B"H2PtCl, amor-

phous pp changing to a crystalline powder

(a) Di oxy-di-(Py 3)-quinolyl C₁₈H₁₂N₂O₂

[239°] Made by potash fusion from diquinolyl (a) disulphonic acid (Weidel a Glaser, M 320) Minute needles, insol water and alcohol, sol zylene — B"HCl yellow needles B"H_PtCl, red plates
D1-acetyl derivative C18H10Ac2N2O2

[170°] Rhombohedral crystals

(β) Di oxy-di-(Py 3)-quinolyl [above 305°] Made by potash fusion from diquinolyl (8) di sulphonic acid (W a G) Crystalline powder (from alcohol), v sol alkalıs

Di acetyl derivative [216°] Plates Tetra oxy diquinolyl Di ethyl derivaof the anhydride C22H18NO2 se O(CoH4(OEt)N)2. A base which apparently has this constitution is prepared by heating $C_{12}H_4(NH_2)_2(OEt)_4$ (of p 667) with o nitro phenol, glycerin, and H_2SO_4 It crystallises from ether, gives a green colour with FeCl,, and forms B"H2PtCl, 2aq (Colson, C R 107, 1003)

(Py 8) **OXY-**(Py 2)-**QUINOLYL** METHYL KETONE C11H,NO2 re C6H, CH C CO CH,

[232°] Made by heating a mixture of o amido benzoic aldehyde and acetoacetic ether at 160° (Friedlander, B 16, 1838) Needles, sl sol. Aq OXY QUINOLYL PHENYL KETONE

 $C_0H_4 < CH C CO C_0H_5$ [above 270°] heating o-amido benzoic aldehyde with benzoylacetic ether (Friedlander a Göhring, B. 16, 1838) Sl sol most solvents

a OXY- $(Py\ 8)$ -QUINOLYL-PROPIONIC ACID C₁H₁NO₂ * e (C₂H₂N)CH₂CH(OH) CO₂H. [125°] Formed from (C₂H₂N)CH₂CH(OH) CCl₂ by heating with alcoholic NaOH (Einhorn, B 18, 8465, 19, 906) Orange crystals, sol water and ppd. by alcohol. Yields (C.H.N)CHO on oxidation by KMnO, -NaA' 3aq -AgA'. yellow pp -H2A'2H2PtCl 5aq

β Oxy-(Py 8)-quinolyl-propionic seid C.H. CH OH N=C CF (OH) CH, CO, H [176°] [176°]. Got from its amide, or by the action of Na, CO, Aq on brome quincly propionic acid in the cold (Einhorn, A 246, 176) Colourless prisms, v sol alcohol and HOAc, insol chloroform.-NaA'-AgA' —HA'HCl [188°] White prisms — H_{*}A'₂H_{*}PtOl_{*} [218°] Yellowish red prisms

Methyl ether MeA' [62°] Prisms
A mide [152°] Made by dissolving the hydrobromide of brome quinolyl propionic acid in ammonia in the cold White crystals (from

alcohol)

Lactone (C,H,N) CH CH CO Made by adding an equivalent quantity of Na₂CO₃ to the hydrobromide of bromo quinolyl propionic acid suspended in water (Einhorn, 4. 246, 169) Needles —C₁₂H₂NO₃HCl [138°] — BC.H.N.O. Golden plates (from alc OXY-QUINONE Methyl ether Golden plates (from alcohol)

C.H.O.(OMe) [140°] Prepared by oxidation of oanisdine with K.Or.O. and dilute H.SO. (Mullhauser, B 18, 92d, A 207, 251, Will, B 21, 605) Got in like manner from the methyl ether of amido resoroin (Bechhold, B 22, 2381) Yellow needles, with pleasant smell, sol alcohol, m sol ether and water Cone H.SO. forms a deep blue solution The vapour colours filter paper red Reduced by SO, to C.H.(OH),(OMe) With annine it forms C.H.(NHPh),(OMe)O, crystallising in coppery needles, and forming a dark blue solution in H2SO4 (Schweitzer, C C 1888, 1434) o Toluidine, o xylidine, and diphenylamine form corresponding bodies melting at 239°, 228°, and 120° respectively

Ethyl ether C.H.20.(OEt) [117°] Made by oxidation of C.H.1(NH2)(OEt), with K.Cr.O., and dilute H.SO. at 15° (Will a Pukall, B 20, Yellow needles (by sublimation), m sol

warm water, decomposed by hot water

Dioxy-quinone C_eH₂(OH)₂O₂[5 2 4 1] Formation -1 By boiling the basic sodium salt of dioxyquinone dicarboxylic acid with HCl or H₂SO₄ (Loewy, B 19, 2387) —2 From diamido-resorcin by oxidation to di imido resorcin and treatment of this body with dilute (10 p c) KOH at 70° (Nietzki, B 21, 2374, Böniger, B 22, 1288) —3 By heating C₆H₂(NHPh)(OH)O₂ or tetra-methyl di amido-quinone with KOHAq (Kehrmann, \vec{B} 23, 904)

Properties — Dark yellow needles, almost insol cold water, v sol alcohol. Its alkaline solutions are red. Not melted at 180° May be sublimed Forms a dioxim Cone HNO, forms nitranili acid — Na₂C₂H₂O₄ — BaC₄H₂O₄aq - Na₂C₆H₄O₄ - BaC₆H₂O₄aq

bluish black needles

De-methyl ether Me.A" [c 220°] Ob-ned by methylation Prepared also from tained by methylation C_sH₂(NO₂)₂(OMe)₂ by reduction followed by oxidation with FeCl₃ (Nietzki a Rechberg, B 23, 1216) Got also by oxidation of acetyl-di methyl pyrogaliol C_eH_s(OMe)_s(OAc) (Hofmann, B 11, 332) Yellow needles Yields, on reduction,

colourless C. d., O. [166°]

Diethyl ether C.H. (OEt), O. [188°].

Got by oxidising the diethyl ether of diamidohydroquinone with FeCl. (N a. B.) Sulphur-

yellow plates (from water) Yields a crystalline dioxim CeH2(OEt)2(NOH)2, which may be reduced by SnCl₂ to C₈H₂(OEt)₂(NH₂)₂.

Di - oxy - quinone Di-methyl ether C_sH_s(OMe),O_s [249°] A product of the oxidation of C_sH_s(OMe),[1 2 3] by nitric soid (Will, B 21, 608) Prisms, v sol hot HOAc Maybe sublimed Reduced by SnCl, to C.H.(OH)2(OMe)2

[158°] Gives C_eBr₂(OMe),O₂ [175°] Tri-oxy-quinone C_eH(OH),O₂ Made from tri amido resorcin by the action of FeCl, the resulting amido-di-imido-resorcin being heated with HClAq at 150° (Merz a Zetter, B 12, 2035) Nearly black powder, msol water, sl sol alcohol Yields a crystalline tri acetyl derivative. Ba,A''', nearly black pp -Pb,A''', -Ag,A''' black pp

' Dshydro-Tetra-oxy-quinone C₆(OH),O₂ carboxylic acid' Formed by the action of alcohol, air, and HCl on the black mass containing C.(OK), got by combination of potassium with CO (Lerch, A 124, 20) Formed also by atmospheric oxidation of a solution of hexa-oxy benzene (Nietzki & Benckiser, B 18, 507, 1836, 1855) It is also a product of the action of HNO, on mosite (Maquenne, A Ch [6] 12, 112) Steel-blue monoclinic needles and plates, v sol. alcohol and hot water, al sol ether Oxidised in alkaline solution by the air to croconic acid. in alkaine solution by the an interest the compound $C_6(OH_2O_4(NPh))NH_2Ph$, crystallising in modules, with green lustre Phenylene-ored needles, with green lustre Phenylene-o-diamine yields C₁₂H₂N₂O₄, sol HClAq (Kehr mann, B 23, 2448) o Tolylene diamine forms black crystals of $C_6O(OH)_3 \ll \frac{N}{NH} > C_7H_6$ (Nietzli a Kehrmann, B 20, 3150) — $K_2C_6H_2O_6$ stable in the air — $K_4C_6O_6$. Readily oxidised by air to $C_6(OK)_2O_4$ — Na $C_6H_2O_6$ dark needles with metallic lustre Sl sol water, forming a darkyellow solution - BaC, H,O, (dried at 100°): dark red pp

Di-acetyl derivative C₆(OH)₂(OAc)₂O₂[2 5 3 6 4 1] [205°].

plates, sl sol water

Tetra benzoyl derivative C_c(OBz), O₂. Yellow needles, sol hot BsCl (Maquenne, Bl [2] 48, 64, C R 104, 1719) Anilide C_c(OH), O(NPh) Made from

C₆(OH)₆, annline, and alcohol Red plates with golden lustre, v sl sol ordinary solvents
References — Di bromo and Di chloro, ds-

oxy quinone

OXY-QUINONE OXIM v NITROSO RESORCIN DI-OXY-QUINONE DICARBOXYLIC ETHER C₀O₂(OH)₂(CO₂Et)₂ [151°] Formed by passing dry nitrous acid gas into an ethereal solution of di oxy terephthalic ether (Hantzsch a Loewy, B 19, 26, 2393, 20, 1306, 1311) Got also by dissolving C₂Cl₂O₂(CO₂Et)₂ in NaOHAq, and by atmospheric oxidation of tetra-oxy-terephthalic ether in presence of NaOHAq (Böniger, B 22, 1284) Greenish-yellow monoclinic prisms (from alcohol) or yellow triclinic plates (from xylene), sl sol. cold water Acid to litmus Its solu-tions are yellow Has no action on phenyl cyanate (Goldschmidt, B 23, 265) SO, yields C₀(OH)₀(CO₂Et)₂. Hydroxylamine produces C₀O₄(ONH₂OH)₄(CO₂Et)₂[170°] Phenyl-hydrax-ine forms C₂O₄(ON₂H₂Ph)₂(CO₂Et)₂[184°] Hot NaOHAq yields an amorphous sodium salt Na, C, 2HO, 2aq, decomposed by hot HClAq yield-

[174°] Needles (from HOAc) (Böniger, B 22,

OXY-QUINOXALINE Dihydride

C₆H₄<NH CH₂ N=COH [c 130°] Made by reduction of o nitro phenyl amido acetic acid with tin and HCl (Plöchl, B 19, 8) Prisms (containing aq), sol alcohol, ether, acids, and alkalis Melts at 94° when hydrated

D1-oxy-quinoxaline C_sH_sN_sO₂ is C₆H₄<N_COH Formed by heating Formed by heating with HCl at 150° the compound of phenylene o diamine and cyanogen (Bladin, B 18, 674, Bl [2] 42, Needles (containing aq), sl sol water Not melted at 290°

DI-OXY DIQUINOYL C₆H₂O₆ re C₆(OH),O, Rhodrsonre acrd 'Carboxylic acrd' Formed Formed by treatment of C6(OK)6 with dilute alcohol and air (Heller, A 24, 1, 34, 232, Lerch, A 124, 32, Will, A 118, 189) Formed also by atmospheric oxidation of $C_sO_2(OK)_4$, and by reduction of CoO, with SO2 (Nietzki a Benckiser, B 18, 513, 1838, 20, 323, 23, 3136) The hydroxyls are probably in the o- position Colourless crys tals, forming a colourless aqueous solution

Reactions -1 Oxidised by HNO, to triquinoyl C₂O₆ -2 Air and Na₂CO₃Aq yield crocomic acid -8 Phenylene o diamine forms redbrown needles of the azine $C_0H_4N_2C_6(OH)_2O_2$ (Nietzki a Schmidt, B 21, 1227) —4 Tolyleneo-diamine forms $C_6(OH)_2O_2N_2C_1H_6$, which crys tallises from HOAc in yellowish brown needles

Salts -Na₂C₆O₆ violet needles, forming an orange aqueous solution - K2C6O8 red powder, or small blue black needles

DI-OXY RICINOLEIC ACID C18H34O5 oxyolesc acid [64°] Made from ricinolesc acid and H₂SO₄ (Liechti a Suida, B 16, 2455) Insol

water, v e sol alcohol OXY-SALICYLIC ACID v DI OXY BENZOIC ACID

OXYSALTS This name is sometimes used to distinguish salts which contain O from those which do not, ie it is applied to salts which are not haloid salts (including cyamides), thio (or sulpho-) salts, nor salts of acids composed of H, halogen, and metal or non metal (v Salts in vol 1v MMPM

OXY SEBACIC ACID C, H, O, [143°] Made by boiling di bromo sebacic acid with water (Claus a Steinkauler, B 20, 2886) Granules, m sol cold water - Na2A" crystalline powder, w e sol water

Di-oxy-sebacic acid C₁₀H₁₆O₆ [130°] Made from di bromo sebacic acid, water, and Ag₂O (C a S) Nodules, v e sol water — Na₂A' sol water

DI-OXY SHIKIMIC ACID Dihydride CH(OH) CH(OH) CH(OH) CO₂H (156°) [a]_D = -28°. Formed from bromo shi

kimolactone and baryta (Eykman, B 24, 1294) Long needles, m sol cold water

OXY-SORBIC ACID C.H.O. [85°] Made from pyridine (a) carboxylic acid by treatment

with sodium amalgam (Weidel, B 12, 2001). Very deliquescent needles Reduces Fehling's solution —BaA'2 —CdA'2 a-OXY-STEARIC ACID C18H36O3 26

C₁₈H₃₈ CH(OH) CO₂H [81°] (G, [85°] (S) S (alcohol) 9 63 at 20°, 2 3 at 20° (S)

Formation -1 A mixture of H₂SO₄ (1 mol) with oleic acid (1 mol) at 0° yields $C_{16}H_{25}$ CH(SO₄H)CO₂H, a liquid acid soluble yıelds ' in ether, water, and alcohol, and forming the salts K_2A'' , Na_2A'' , $(NH_4)_2A''$, $Ba(HA'')_1$, and $Cu(HA'')_2$. This and is decomposed by boiling dilute acids into H₂SO₄ and a oxy stearic acid (Gentel, J pr [2] 37, 74, cf Fremy A 33, 15, Ssabanejeff, B 19, 239 Ref , Saytzeff, J p [4] 35, 369) -2 By the action of moist Ag₂O on 10do stearic acid prepared from oleic acid, P, and I (Saytzeff, J pr [2] 33, 310, 35, 378, Bl [2] 47, 169)

Preparation -H2SO4(32g) 18 gradually added to olive oil (88 pts) in the cold, and the mixture boiled with alcoholic potash The pro duct is acidified by hydrogen chloride, and the separated acids crystallised from ether (Geitel) In this preparation there is also formed the acid (C₁₆H₂₈ CH(CO₂H))₂SO₄ [24°], which yields a oxy stearic acid on boiling with dilute acids

Properties - White six sided plates, m sol alcohol, v sol ether At 200° it forms a syrupy anhydride, which is also formed by heating with fuming HClAq at 100° for 12 hours Does not unite with Br Reduced by HI to stearic acid

Salts—NaA'—CaA', small orystals (G)—CaA', aq (C a S)—BaA', —ZnA', —CuA', green powder—PbA', —AgA'

γ Oxy-stearic acid The lactone C₁₄H₂₉ CH(OH) CH₂ CH₅ CO H C₁₈H₂₄O₂ [48°] is one of the products of the action of H2SO4 on oleic acid After boiling with potash it yields Ca(C18H35O3), and Pb(C₁₈H₂₈O₂)₂, whence acids at once set free the lactone

Di oxy-stearic acid $C_{18}H_{36}O_4$ [136°] S (alcohol) 6 at 19° S (ether) 19 at 18° (Spiri donoff, J pr [2] 40, 243) Formed from dibromo stearic acid (oleic acid dibromide) by treatment with moist Ag₂O (Overbeck, A 140,72) Got also by boiling oxyoleic acid with potash (O) Prepared by oxidising cleic acid with alkaline KMnO₄ (Saytzeff, *J pr* [2] 31, 541, 33, 304, *Bl* [2] 45, 255) Probably identical with a di oxy steam acid [181°] got by oxidising tallow with KMnO₄ (Groger, B 22, 620) Tables, insol water, v sol hot alcohol, v sl sol ether verted by HI into iodo stearic acid Reduced by alcohol and zinc to stearic acid under 100 mm it gives an acid [c 79°], which may be its anhydride $C_{18}H_{34}O_3$. This acid forms the salts $C_{18}H_{33}AgO_3$ and $C_{18}H_{38}NaO_3$. Yields octore, sebacre, and azelare acids on oxidation by KMnO

Salts -NaA' - KA' - CaA' aq - BaA'. ZnA' --- AgA'

Di-acetyl derivative Syrup, sol ether Methyl ether [106°] 8 at 185° S (ether 104 at 19° S (alcohol) 3 45 9° Plates

(Saytzeff, J pr [2] 33, 315) More sol alcohol and ether than the preceding isomeride -NaA' | Yields a benzoyl derivative C.H. (OBz) CO CH.

Di oxy stearic acid C18H26O4 [78°] Got by the action of A 5,0 on the dibromide of iso-oleic ac'd [45°], whi h is formed from iodo stearic acid and alcoholic potash (Saytzeff, J pr [2] 37, 276) Crystalline powder, v sol alcohol and ether HI yields an iodo stearic acid ieduced by tin and HCl to stearic acid

Tri-oxy stearic acid C18H38O4 ' Rucinolic acid' [141°] Occurs among the products of the oxidation of castor oil with alkaline I MnO₄ (Hazura a Grussner, M 9, 476)—KA'

Tri oxy stearic acid C18H36O5 'Ricinisolic acid' [111°] Occurs together with the prece ding isomeride, among the products of oxidation

of castor oil by KMnO (H a G)
Tri oxy stearic acid C₁₆H₂₆O₅ [115°] Formed
by oxidising ricinelaidic acid with alkaline KMnO₄ (Hazura a Grussner, M 10, 199) Tri metric prisms, insol cold water, v sol HOAc and ether

Tetra oxy stearic acid C₁₈H_{3e}O₈ i.e C₁₈H_{3r}(OH)₄O₈. Sativic acid [173°] duct of the oxidation of linoleic acid by alkaline KMnO₄ (Hazura, M 9, 190) Long prisms Converted by HI into C₁₈H₃₄I₂O₅ and finally into stearic acid

Hexa-oxy stearic acid C18H28O8 Linusic •acıd [203°] Got by oxidising linoleic acid with alkaline kMnO, being derived from lin olenic acid, which is present in linoleic acid (Hazura, M 7, 637, 8, 155, 267) Minute needles (from water) More sol water and less sol alcohol than sativic acid Yields a hexa acetyl derivative

Hexa oxy stearic acid C18H26O6 Isolinusic acid [175°] Occurs in small quantity, to gether with sativic and linusic acids, in the pro duct of the oxidation of linoleic acid by alkaline KMnO, Needles, insol ether, v sol hot water Forms a hexa acetyl denvative, sl sol ether

OXY STILBENE v OXY DI PHENYL ETHYL

DI-0 OXY-DI STYRYL DIKETONE C, H14O3 re CO(CH CH C₆H₄OH)₂ [160°] Got by heat mg the glucoside with dilute H₂SO₄ Brownish

powder, sol alcohol

GlucosideCO(CH CH C₆H₄ OC₅H₁₁O₅)... Formed, together with the compound [257°] CH, CO CH CH C,H, OC,H,1O,, by condensation of helicin with acetone in presence of a little alkali (Tiemann a Kees, B 18, 1967) Colour less crystals (containing aq), sl sol alcohol, nearly insol water, insol ether

Tetra, oxy di styryl ketone Di methylene derrvative CO(CH CH C,H, O,CH,), [185°]
Made from piperonal, acetone, and NaOHAq
(Haber, B 24, 617) Yellow needles, insol water, m sol alcohol Colours H,SO, a deep

O OXY STYRYL METHYL KETONE

[139°] C10H10O, te C2H4(OH) CH CH CO CH, Got by hydrolysis of its glucoside by emulsin (Tiemann a Klees, B 18, 1964) Formed also from salicylic aldehyde, acetone, and dilute NaOH (Harries, 13 24, 5180) Long needles (from alcohol), sl soi water FeCl, colours its aqueous solution blue Sodium amalgam reduces tt to C.H. (OH) CH CH CH(OH).CH, [48°].

[88°], an oxim C,H₄(OH) C(NOH)CH₂ [85°], and a phenyl hydrazide [160°]

Glucoside CH₂ CO C,H₂ C,H₄ O(C,H₁₁O₂)

[192°] Made by adding a few drops of caustic soda solution to a mixture of acetone and helicin C_eH₄(OC_eH₁₁O_s) CHO Slender needles (containing aq), v sol hot water Lævorotatory Yields an oxim [173°]

p-Oxy-styryl methyl ketone Methyl derivative C.H. (OMe) CH CH CO CH, [78°] Made by allowing anisic aldehyde, acetone, and aqueous NaOH to stand in the cold (Einhorn a. Grabfield, A 243, 363) Plates, v sol alcohol

D1-oxy styryl methyl ketone Methyl derivative CH, CO CH CH C,H,(OH)(OMe) [1 4 3] Got from its glucoside by the action of emulsin Yellow needles, v 30l alcohol

Glucoside CH_s CO CH CH C₆H_s(OMe)(O C₅H₁₁O₅) [207°]. Got by heating the glucoside of vanillin with acetone and NaOHAq (Tiemann, B 18, 3491) Pale yellow needles (containing 2aq), m. sol water Lævorotatory

Methylene derivative CH, CO CH CH C6H, O CH2 [107°] from piperonal, acetone, and NaOHAq (Haber, B 24, 618) Prisms, sl sol warm water Changed by steam into an isomeride (?) [111°] Yields a yellow oxim [186°] and phenyl hydrazide [160°] The isomeride [111°] yields a colourless oxim [183°] and phenyl hydrazide [163]

DI-OXY-STYRYL m PYRAZOLE C11H12N2O4 16 CO NH CH CH CHPh Di oxy styryl-gly- $[172^{\circ}]$ oxaline Styryl hydantoin Made by the action of boiling dilute hydrogen chloride upon CHPh CH CHCy NH CO NH2, which is got from cinnamic aldehyde cyanhydrin, and urea (Pinner a Lifschutz, B 20, 2353, 22, 685) White plates, changing on fusion to an isomeride [195°

Reactions -1 On heating with alcoholic potash it yields the isomeric C(NH) < O-CH C-H-Ph which decomposes at 300° and, with KOH and Which decomposes 2. ΓtBr, yields C(NH) < NEt CO $_{\rm O-CH}$ C₂H₂Ph 2 Alcoholic potash and EtBr at 100° from CO NEt CO NEt CO P. 1900 Bromine in Promine CHCl₂ forms $C_{11}H_{10}N_2O_2Br_2$ [200°] Bromine
uater produces CO < NH CO
NH CH CH(OH) CHBrPh [220°], whence NaOHAq forms tri oxy styrylmetapyrazole CO NH CO CH2Ph talline powder [185°]

Acetyl derivative CO NAC CO

5°] Small white prisms o-OXY-STYRYL-PYRIDINE C₁₃H₁₁NO *** $C_{\circ}H_{\bullet}(OH)$ CH CH $C \leqslant_{N}^{N} CH > CH$ Formed by heating (a) methyl pyridine (10 g) with salicylic aldehyde (13 g) and water (7 g) at 140° (Butter, B 23, 2697) Small crystals (from dulute alcohol) Yields a dibromide Reduced by Na and alcohol to C₂H₄(OH) C₂H₄ C₂H₁₀N [94°] Salts—B'₂H₂PtCl [188°]—B'HHgCl, [c 170°] Salts of the ethyl derivative (C,H, (OEt)N),H,HgCl [92°] Light-yellow

| College | Coll anisic aldehyde and methyl pyridine (Schuften, Plates — B'2H2PtCl B 23, 2719) Yellow plates

P-OXY (Py 3)-STYRYL QUINOLINE

C'H' CH CH CH C'H' OH. C, H, NO s.c. [258°] Formed from p-amido-styryl-quinoline by the diazo-reaction (Bulach, B 22, 286) Formed also from p oxybenzoic aldehyde, quinaldine, and ZnCl₂ (Wallach, B 16, 2009) Yellow plates

o-Oxy-(Py 1) styryl-quinoline [215°] Made from salicylic aldehyde, lepidine, and KHSO, (Heymann a Königs, B 21, 1429, 2172) Yellow

erystals

m-Oxy-(Py 1)-styryl-quinoline. [255°] Got from m amido-styryl quinoline Brownish-

yellow crystals (from alcohol)

p-0xy-(Py 1)-styryl quinoline [249°] Got from p-oxy benzoic aldehyde, lepidine, and KHSO, (H. a K) Yellow crystals (from alcohol)

OXYSUBERANIC ACID C₈H₁₄O₅ 1.6 C₇H₁₂(OH) CO₂H [90°] Made from suberone eyanhydrin and cone HClAq (Spiegel, A 211, Tables (containing \frac{1}{2}aq) Melts at 50° hydrated V e sol alcohol and hot when hydrated

OXYSUBERIC ACID C.H.,O. [112°] Made by boiling bromo-suberic acid with NaOHAq (Hell & Rempel, B 15, 149, 18, 817) Nodules (from ether) HNO, oxidises it to adipic and oxalic acids —MgA" aq —CuA" —ZnA" 2½ aq — Ag.A" crystalline pp

Ethyl derivative C₆H₁₁(OEt)(CO₂H)₂ Made from bromo suberic acid and alcoholic potash. Syrup, v sol water and alcohol—BaA"—ZnA"—PbA"—Ag₂A" amorphous pp
Oxy-isosuberic soid C₅H₁₄O₅ A sticky mass

got by saponification of its ether, which is a product of the action of silver on bromo butyric ether (Hell a Muhlhauser, B 13, 477) HIAq at 160° reduces it to β isosuberic acid —Ag₂A"

Di-exy-suberic acid C₅H₁₄O₆ Made from di-brome-suberic acid and KOH (Gay a Gay-

Lussac, A. 155, 251) Amorphous

Di-ethyl derivative CaH10(OEt)2(CO2H)2. Made from di bromo suberio acid and alcoholio potash (H a. R) Syrup, v sol water, alcohol, and ether —Ag,A" amorphous pp

OXY-SUCCINIC ACID v MALIC ACID

Di-oxy-succinic acid v Tabtaric acid Tetra-oxy-succinic acid

C.H.O. i.s. CO.H.C(OH), C(OH), CO.H. or CO.H.CO CO.H. 2aq Di-oxy tartaric acid Carboxytartronic acid [98°] Formed by passing nitrous acid into an ethereal solution of protocatechuic acid (Grüber, B 12, 514), of pyrocatechin (Barth, M. 1, 869), of guaiacol (Herzig, M 3, 825), or of 'nitro'-tartanc acid (Kakulé, A 221, 240). The free acid is got by decomposing the dry sodium salt in dry ether with HCl gas (W L. Miller, B 22, 2015). White erystals, v. sol. water The salt Na₂O₂H₂O₂2aq is nearly maol water It splits up on heating into OO₂ and sodium tartronate. With NaHSO₂

at 90° it yields glyoxal (Hinsberg, B 24, 3235). The salt Ba₂(C₄H₂O₂), aq is a crystalline pp. HClAq and zinc reduce it to a mil ture of racemic and mactive tartaric acids Yields hydantoin when the Na salt is rubbed up with urea and dilute HClAq at 55° (Anschutz, A 254, 258)

Ethyl ether Thick liquid (Anschutz, A 261, 130). Converted by urea into the ureide C₁₀H₁₄N₄O₆, which crystallises in needles, sl sol

cold water, decomposing at 245°

CO2H C(NOH) C(NOH) CO2H (β) -Oxim[145°_150°] Got from the Na salt, hydroxyl amine and HCl Colourless prisms, v e sol water and alcohol, insol benzene (Müller, B 16, 2985, Söderbaum, B 24, 1223) After crystallisation from water it melts at 70°-75° It yields the salts CaA" 4aq and Ag2A" and a crystalline discetyl derivative, v sol water Conc HClAq converts the oxim into an isomeride [145°-150° crystallising in nodules, which are v e sol water and yield the salts CaA" Saq and Ag2A" aq Ac.O decomposes this (a) oxim into cyanogen and CO2

Phenyl hydraside C1.H.N.O. 16 CO₂H CO C(N₂HPh) CO₂H Monophenylisme dioxytartaric acid [218°] Made by mixing a solution of the soid (1 mol) with phenyl hydraz me (1 mol) dissolved in HClAq (Ziegler a Locher, B 20, 835) Feathery needles, insol cold water, v sol hot alcohol Coloured red by FeCl_s - BaC₁₀H_eN₂O₆3aq '- Na₂A'' - Ag₂A'

orange yellow pp Di-phenyl di-hydrazide CO₂H C(N₂HPh) C(N₂HPh) CO₂H Diphenylisine dioxytartaric acid [above 200°] Made from tetra-oxy succinic acid (1 mol) and phenyl hydrazine (2 mols) Orange-yellow powder, v sl sol On heating with water, v sol warm alcohol

Ac₂O it yields $O<_{OO\ C\ N_2AcPh}^{CO\ C\ N_2HPh}$ [c 234°], which crystallises in red needles, v sol (NH₄)₂A" colourless plates — (NH₄)HA" brick red needles With silver nitrate it gives

 $\Delta_{gN} <_{CO}^{CO} \stackrel{C}{C} \stackrel{N_2HPh}{N_2HPh}$ of a vermilion colour

Na₂A" lemon-yellow plates —NaHA" brick red needles —The ethyl ether C₂₀H₂N₄O₄ [121°] is got from phenyl hydrazine and tetra oxy succinic ether (A a G), it forms canary yellow crystals

Di-p-sulpho di phenyl-di-hydraside CO.H.O(N.H.O.H.SO.H) C(N.H C.H.SO.H) CO.H Formed from sodium tetra-oxy succinate, sodium phenyl-hydrazine p-sulphonate, and HClAq The Na salt is an orange-yellow powder, v sol water, insol alcohol, and is used as a yellow dye (tartrazıne)

Dr-phenyl-hydraside [1589] Made from the acid and N₂H₂Ph₂. Yellow pp, turning

blue in the air

Tetra phenyl-di hydrasids
CO_HC(N₂Ph₂) C(N₂Ph₃) CO₂H [177°] Made
from the acid (1 mol.) and diphenylhydrasine
(2 mols) (Ziegler a. Locher, B 20, 841).
Yellowish plates (from hot alcohol), insol. water. Cone H.SO, forms a red solution, becoming green On fusion with resorein it gives a crimson mass, coloured blue by NaOH, hydroquinone and pyrogallol give green and blue masses respectively. Bromine gives a crystalline bromederivative Ac₂O forms O CO C N₂Ph₂ [222°] crystallising in ruby red prisins with 5.00 C N.Ph. Converted into the imide NH CO C N.Ph. erystallising in ruby red prisms with green lustre [192°] by NH, -Na, A" rosettes of needles (from water) or plates (from alcohol) -CuA" -PbA".

m-Nitro-phenyl-hydraside 775°1 Made by using m nitro phenyl hydrazine (Bischler a Brodsky, B 22, 2814) Sl sol hot

water and alcohol

Di-m notro di-phenyl-dihydraside [c 2000] Made from m nitro-phenyl-hydrazine (2 mols) and tetra oxy-succinic acid (1 mol). Sl. sol hot water

OXYSULPHIDES Compounds of an element, or positive compound radicle, with O and The term is generally restricted to compounds of metals with O and S Oxysulphides of metals are not numerous, and they have not been much studied They are produced in various reactions, of which the following are the chief by acting on the sulphide with water, e oxysulphide of Ba, by heating the oxide with S, eg Bi oxysulphide, by boiling the oxide and sulphide with water, eg Ca oxysulphide, by partially reducing the sulphate by H, eg oxysulphides of Co and Mn, by heating the oxide in H₂S, or by passing H₂S into an aqueous solution of the oxide, e g oxysulphides of Fe and Os, by adding a little alkali sulphide to the solution of a salt, eg Cu oxysulphide MMPM

OXY-SULPHO-BENZOIC ACID C,H,SO, 18 C.H. (OH)(SO.H) CO.H Sulphosaliculic acid Made by sulphonation of salicylic acid (Mendius, A 103, 45, Remsen, A 179, 107) Long thin needles, v e sol water and alcohol Gives a reddish-violet colour with FeCl. Yields phenol and salicylic acid on fusion with potash

NaHA" 2aq — Na₂A" 3aq — KHA" 2aq —

K₄A" 2aq — K₁HA", aq — KNaA" 4aq — CaA"aq

Ba(HA"), 4aq — MgA" 3aq — ZnA" 3aq

PbA" — CuA" — Cu₂A"(OH), aq — Ag₂A" aq

crystalline powder, v sol hot water

Ethul ather, Et A" [53°] Crystals

Ethylether Et.A" [58°]. Crystals

Oxy-sulpho bensoic acid

C₆H₃(OH)(SO₃H)(CO₂H) [4 3 1] Made from poxy benzoic acid by treatment with SO₂ (Kölle, A 164, 150) or by digesting with H_2SO_4 at 100° (Klepl, J pr [2] 28, 196) Deliquescent needles, v e sol water and alcohol, msol ether FeCl, gives a red colour Potash-fusion yields proto-catechuic acid —KHA" aq crystals, sl sol water (Klepl) —K₂A" aq (Kölle) —K₃C,H₃SO₅ 2aq (Kölle) —BaA" 4aq —Ba₂(C,H₂SO₂), amorphous (Kölle) —CdA" 8aq —Ag₂A", small prisms

Methyl derivative C_eH₄(OMe)(SO₂H)(CO₂H) Made from fuming H.SO, and anisic acid at 160° (Zervas, A 103, 838, Limpricht, Gm 13, 128) Needles, insol ether -BaA" aq -PbA" aq: needles, sl sol Aq

Oxy-sulpho-benzoic acid C.H.(OH)(SO.H)(CO.H) [4 2 1] Formed by the diazo-reaction from (4,2,1)-amido sulpho-benzoic acid (Hedrick, Am 9, 416) Crystalline, sol water, alcohol, and ether —Ba(HA"), insol dilute HOAc — BaA" — CaA" baq triclinic prisms, sol hot water.—CoA"7aq —ĈdA"8aq -ZnA" Saq (Pisanello).

Imide of the ethyl derivative

 $C_eH_s(OEt) < CO \\ SO_2 > NH$ [258°] Made by oxidising C.H.Me(OEt) SO,NH, with KMnO, and ppg with HCl (Remsen a Palmer, Am 8, 227) Concentrac groups of needles -KC.H.NSQ. -AgC,H,NSO, lustrous needles, sl sol water. Oxy-sulpho-benzous acid

Cwy-suppo-censor acid
CH₂(OH)(SO₂H)(CO₂H)[3 4? 1] Formed from
m oxy-benzor acid and SO₂ (Barth, A 148, 38,
Senhofer, A 152, 102) Yellowish green needles
(containing 1½aq), v sol alcohol Coloured red
by FeCl₂ Yields protocatechine acid and an
acid [189°] when fused with potash—BaA"4½aq
—Cd(HA"), 2aq—Pb₂(C,H₂SO₆)₂ reddish amor
phous mass phous mass

Oxy-sulpho benzoic acid

C.H. (OH)(SO.H) CO.H Got by dissolving m diazo benzoio acid in warm H.SO, (Griess, Z 1864, 538) White laminæ (from water) Perhaps identical with the preceding acid -BaA".

Oxy-disulpho-benzoic acid C,H2(OH)(SO,H),CO,H [146°] Made from salicylic acid and ClSO, H at 180° (Pisanello, G 18, 346) Deliquescent needles (containing 4aq) Gives a red colour with FeCl₁—Na₂A''' 3aq—Ca₂A'''₂12aq—Ba₂A'''₂6¹₂Aq prisms, sl. sol water—Pb₂A'''₂10aq—Cd₂A'''₂18aq—Cu₂A'''₂12aq—Zn₂A'''₂15aq plates

Oxy-disulpho-bensoic acid C,H₂S₂O₃ Got

by boiling trisulpho m oxy benzoic acid with BaCO, (Kretschy, B 11, 862) —Ba, A", 8aq

Oxy-trisulpho-benzoic acid C_aH(OH)(SO_aH)₃CO₂H Made by heating m-oxybenzoic acid with H₂SO₄, SO₄, and P₂O₅ at 250° (Kretschy, B 11, 858) Hygroscopic syrup (containing 4aq at 100°) FeCl₃ gives a red colour — K₅C₂HS₃O₁₂2sq monoclinic prisms —K₄A¹ 2sq Pb₅(C₂HS₃O₁₂), 6sq — Pb₂A¹ 8sq —Cd₂A¹ 3sq —

Ba A' 4aq colourless plates Di-oxy-sulpho-benzoic acid C₂H₂(OH)₂(SO₃H)CO₂H Formed from (4, 2, 1) di oxy benzoic acid and H.SO, (Zehenter, M 2, 468) Hygroscopic needles (containing 2aq) FeCl_s colours its aqueous solution red —
Salts — K_sA'' 8½aq — BaA'' 2aq — PbA'' 2aq —
Cu_s(C,H_sSO_s), 5aq — Ag_sA'' 2aq needles
Di oxy-sulpho-benzoic soid

C_eH₂(OH)₂(SO₂H)(CO₂H)[5 2 x 1] Made by heating (5, 2, 1)-di oxy-benzoic acid with H₂SO₄ and P₂O₅ at 180° (Senhofer a Sarlay, M 2, 454) Needles -K,A" aq -Ba(HA"), 8 aq -BaA" 2aq -PbA" 2aq crystalline powder

OXY SULPHO-ISOCUMINIC ACID

CMe₂(OH) C₆H₄(SO₅H)(CO₅H) Made by oxidising the sulphonic acids of cymene and m-isocymene by KMnO, (B. Meyer, A 220, 7, 29) K.A" 5aq —BaA" aq · minute plates —PbA"

OXY - SULPHOCYANO - ACETOACETIC Anhydride O(CAc(SCy) CO,Et) ETHER. [c 168°] Made by heating equivalent weights of barrum sulphocyanide and dichloro-acetoacetic ether (207°) (Zürcher, A 250, 293) crystalline powder (from alcohol), insol. ether.

OXY-SULPHO-NAPHTHOIC ACID

C₁₀H₄(OH)(SO₂H) CO₂H Made from (a)-oxynaphthoic acid and H₂SO₄ at 60° (König, B 22, 787, 28, 806) Needles (containing 5aq), v sol water and alcohol Its alkaline solutions fluoresce blue HNO, yields di-nitro-naphthol [1880 Diazobenzene chloride forms the azo-compound $\begin{array}{ll} \textbf{C}_{19}\textbf{H}_{a}(O\textbf{H})(N_{2}\textbf{Ph})SO_{2}\textbf{H} - Na\textbf{H}\textbf{A}'' & needles, & \textbf{v} \\ \textbf{sol} & \text{water} - Na_{2}\textbf{A}'' xaq - Ba(\textbf{H}\textbf{A}'')_{2} \end{array}$

Oxy-di-sulpho-naphthoic acid

 $C_{10}H_4(OH)(SO_3H)_2CO_3H$ Formed from (a) oxynaphthoic acid and fuming H_2SO_4 (K) Stellate groups of needles (containing 4aq)— K_2A'' — $Ba_3(O_1H_1S_2O_2)_2$ needles, m sol water OXY-SULPHYDRO-ALLYL-QUINAZOLINE

C.H. CO N C.H. Allylthrobenzoylurea [199°]
Formed from o amido benzamide and allyl thio carbimide (Stewart, J pr [2] 44, 416) Needles

Its henzene solution fluoresces blue

XY SULPHYDRO DI-METHYL-GLYOXAL-

INE Dr methyl derivative

NMe C(OMe) CMe Formed from di methylthio-hydantoin [167°], alcoholic potash, and MeI (Marckwald, B 24, 3293) Syrup —B'HCl syrup —B'H₂SO₄ crystalline —B'₂H₂PtCl₆

The isomeride NMe CO C(SMe) N formed from tri methyl thiohydantoin, alcoholic potash, and MeI yields the crystalline salts B'H SO₄ [138°] and B'₄H₂PtCl₆ [150°]

0XY - SULPHYDRO PHENYL - METHYL-GLYOXALINE Dt-methyl derivative NPh<C(OMe) CMe [90°] Formed from phenyl methyl thiohydantoin, alcoholic KOH, and MeI (Marckwald, B 24, 3290) Crystals — B'HCl [140°] — $B'_{\rm C}H_{\rm p}N_{\rm p}$ O, [192°]

The isomeric compound NPh < $^{\rm CO}_{\rm C(SMe)}$ $^{\rm CMe}_{\rm C(SMe)}$ $^{\rm CO}_{\rm C(SMe)}$ $^{\rm CO}_{\rm CO}$ $^{\rm CO}_{\rm C$

OXY-SULPHYDRO-PHENYL QUINAZOL-INE C₈H₄ CO NPh [199°] Formed from oamido benzamide and phenyl thiocarbimide (Stewart, J pr [2] 44, 416) Satiny tables OXY SULPHYDRO QUINAZOLINE

C_oH_s CO NH NH [281°] Formed from o amido benzamide and thio urea (Stewart, J pr [2] 44, 416) Nodules (from alcohol)

OXY SULPHYDRO-THIAZOLE C₃H₃NS₂O 2 e

NH CS S
CO CH₂ [167°] Formed by heating
NH C(NH) S
with CS₂ in alcohol at 160°
(Miolati, A 262, 84) Formed also from chloro acetic ether, ammonium dithiocarbamate, and

alcoholic HCl, and from sulphocyanoacetic ether by successive treatment with H₂S and HCl OXY-SULPHYDRO c-TOLYL-METHYL GLY-OXALINE Di methyl derivative

C.H.MeN C(SMe) N [120°] Got from otolyl-methyl-thiohydantom, alcoholic potash, and MeI (Marckwald, B 24, 8292) Plates, v sol alcohol Yields the following salts B'HCl [120°], B'HPtCl, B'H,SO, [205°], B'HNO,, and the parate B'C.H.,No, [200°]

The isomeric C_eH₄MeN CO CO if the salts B'HCl [118°], B'₂H₂PtCl_e, B'H₂SO₄ [208°], and B'C_eH₂N₂O, [212°].

Oxy-sulphydro-p-tolyl-methyl-glyoxaline Di-methyl derivative [109°] Plates Yields B'HCl [123°], B'₂H₂PtCl₆, and B'C₆H₃N₃O₇ [180°]

The isomeric [4 1]C₆H₄MeN $< \frac{C(8Me)}{CO} \stackrel{N}{\longrightarrow} CMe_2$ yields B'H₂SO₄ [210°], B'₂H₂PtCl₅ [152°], and B'C₆H₃N₃O₃, decomposing at 190°

DI-OXY TARTARIC ACID v Tetra oxysuccinic acid

OXY TEREBIC ACID C,H, O, [100°-120°] Made by boiling chloro terebic acid with water and CaCO, (W Roser, A 220, 2^4) Syruy, crystallising with difficulty, v sol warr—CaA'₂—AgA' needles, v sol water

OXY TEREPHTHALIC ACID C, H, O, te C, H, (OH) (CO, H), E Formed by the diazo reac ton from amide terephthalic acid (De la Rue a Müller, Burkhardt, B 10, 144, 1273) Prepared also by potash fusion from bromo terephthalic acid (Fischli, B 12, 621), from oxy aldehydo ben zoic acid (Tiemann a Landshoff, B 12, 1335), from p xylenol, from carvacrol, and thymol (Jacobsen, B 11, 570), from oxy p toluic acid (Hall a Remsen, B 12, 1433), and from run gallic acid (Schreder, M 1, 439)

Properties —Crystalline powder, sl sol water, v sol alcohol Not melted at 300° FeCl₂ colours its solution reddish violet Yields CO₂ and phenol when strongly heated On fusion with NaOH it gives salicylic acid and some p-oxy benzoic acid (Barth a Schieder, B 12, 1260) Yields moxy benzoic acid on heating with HClAq at 120° Forms a di nitro derivative [179°]

Salts —BaA" 3 aq lamına (from water) — Ag₂A" white pp, insol water

Methyl ether Me₂A" [94°] Leaflets Yields an acetyl derivative C₆H₃(OAc)(CO₂Me)₂ [76°]

Methyl derivative C_eH₃(OMe)(CO₂H)₂ [279°] Got by oxidation of methoxy toluic acid and of methyl thymol Small prisms

Methyl ether of the methyl derivative C_sH_{*}(OMe)(CO_.Me)₂ [65°] Concentric needles Ethyl derivative C_.H_{*}(OEt)(CO_.H)₂. [254°] Got by oxidation of the ethyl ether of thymol (Paterno a Canzoneri, G 9, 460) Stellate groups of minute crystals, insol water

Benzyl derivative $C_0H_3(OCH_2Ph)(CO_2H)_2$. [230°-240°] Made from $C_0H_3(ONa)(CO_2Me)_2$ and benzyl chloride, the product being saponified (Baeyer a Tutein, B 22, 2188) Slender needles

Tetrahydride C₆H,(OH)(CO₂H)₂ Got by reducing the acid with sodium amalgam (Baeyer a Tutem, B 22, 2180) Yellowish white reedles, sl sol cold water Coloured bluish violet by FeCl₃ Its methyl ether forms feathery needles [77°] Hydroxylamine converts the tetrahydride into C₇H₁₀O₂(NOH) [170°], while phenyl hydrazine forms C₇H₁₀O₂(N₂HPh) [125°] converted by HClAq into C₈H₄>O₆H, CO₂H, a crystalline

body [230°] giving off a fæcal odour when heated The tetrahydride, heated at 120°, loses CO₂ and forms $C_6H_5O(CO_2H)$, whence NaA' and $C_6H_5(OH)$ Cy CO_2H [130°–140°] may be prepared, the latter body yielding the crystalline acid $C_6H_5(OH)(CO_2H)_2$ on saponification

Di - oxy - terephthalic acid C.H.O. te O₆H₂(OH)₂(CO₂H)₂[5 2 4 1] or CO CH(CO₂H) ун(со'н) со√

Quinone hydro cycarboxylic acid Hydroquin one dicarboxylic acid [above 300°]

Formation —1 By passing a current of air through a solution of the dihydride of its ether (succinyl succinic ether) containing excess of alkalı (Herrmann, B 10, 107, A 211, 335) —

2 By the oxidising action of KMnO₄ on C₆H₂Me(C₂H₂)(OPO₃K)₂, a derivative of thymoquinone, and on C₆H₂Me₂(OPO₃K)₂, a derivative of hydro p xyloquinone (Heymann a Konigs, B 20, 2392) -3 By the action of PCl, on succinylsuccinic ether (Levy a Curchod, B 22, 2108) -

4 By saponifying its ether

Properties -Interlaced needles (containing 2aq) (from water) or yellow plates (from alcohol), sl sol alcohol and ether, v sl sol water Its alcoholic solution shows blue fluorescence FeCl₃ gives a deep blue colour When distilled it yields hydroquinone Bromine water yields Chlorine passed into its tetrabromoquinone alcoholic solution forms tetra chloro quinone (Loewy, B 19, 2394)

Salts -K2A" yellow needles, forming a solution with green fluorescence — KHA" — Na₂A" 2aq — NaHA" 2aq — Na₄A" (OH), 10aq crystals ppd by conc NaOHAq — (NH₄)₂A" 2aq (Duisberg, A 213, 16?) — BaA" — CaA" 5aq —

Ca(HA')₂54q —PbA'' —Ag₂A'' green yellow pp Mono ethyl ether EtHA'' [184°] Made by the action of dilute KOH on the di ethyl ether in the cold Pale yellow needles (from water), sl sol water, alcohol, and ether Ba(EtA")25aq —Ca(EtA")25aq greenish yellow

needles

Dr ethyl ether Et2A" [133°] S (ether) 16 at 20° Prepared by adding bromine to a solution of its dihydride in CS, or to the dihydride suspended in water (Herimann, A 211, 327, B 19, 2229) Formed also by the action of sodium on di bromo acetoacetic ether dis-

solved in ether (Wedel, A 219, 74)

Properties - Greenish yellow trimetric tables (from benzene) or needles (from ether) be sublimed Its alcoholic solution shows blue fluorescence FeCl, gives a bluish green colour Does not react with phenyl cyanate (Gold schmidt a Meissler, B 23, 259) Does not leact with phenyl hydrazine or hydroxylamine alkalis, forming a yellow liquid, from which it is ppd by CO₂, and, as a scarlet pp, Na₂C₁₂H₁₂O₃, by conc NaOHAq Ac₂O has no action at 510°

Reactions—1 Reduced to its dihydride by

sinc and MClAq (Baeyer, B 19, 428) —2 Biomine sapour forms C₈H₂Br₂O₂(CO₂Et), [157°] and afterwards $C_8Br_1O_2(CO_2Et)_2$ (Hermann, B 19, 2234, Böniger, B 21, 1758) -3 Dry nitrous acid gas passed into its solution in absolute ether oxidises it to di oxy quinone dicarboxylic ether (Hantzsch a Loewy, B 19, 26), an intermediate crystalline powder $C_{24}H_{25}NO_{16}$ or C₂₁H₂₃NO₁₆ [148°] giving a violet colour with alkalis being first formed (Loewy, B 19, 2393)

Hydrate of the ether C₁₂H₁₈O₈ is CO₂Et C C(OH), CH,

Formed, together with the ether, by the action of bromine on the dihydride (succinyl-succinie ether) (Hantzsch a Zeckendorf, B 20, 2800) Yellow needles On boiling with alcohol it changes to the ether $C_{12}H_{14}O_e$ [133°] Hydroxylamine reduces it to $C_{12}H_{14}O_e$ [128°]

Di acetyl derivative of the ether C_aH₁(OAc)₂(CO,Et)₂ [154°] Got by the action of AcCl on the ether or on C_aH₂(ONa)₄(CO,Et)₅ (Wedel, A 219, 81, Nef, A 258, 306) clinic crystals Not attacked by Br Its alco-

holic solution is not fluorescent

Di-benzoyl derivative of the ether C_eH₂(OBz)₂(CO,Et)₂ [174°] ether, NaOHAq, and BzCl Made from the Colourless needles (from alcohol) Not attacked by Br in CHCla Conc H₂SO₄ sets free C₈H₂(OH)₂(CO₂Et)₂ Zincdust and conc HClAq form three isomeric di-hydrides C₆H₄(OBz)₂(CO₂Et)₂ melting at 165°, 85°-95°, and 100°-110°

Di methylderivative

C₆H₂(OMe)₂(CO H), [265°] Formed by saponi fication of C₆H₂(OMe)₂(CO Et)₂ (v infra) with alcoholic potash (Nef, A 258, 298) Colourless Its aqueous solution shows bluishneedles violet fluorescence -(NH₄)₂A" sol water Not fluorescent

Di methyl derivative of the ethyl ether C₄H₂(OMe)₂(CO₂Et)₂ [1015°] Made from C₄H₂(ONa)₂(CO₂Et)₂ and MeI at 100° (Nef, A 258, 297) Colourless tables Its solutions show bluish violet fluorescence Not reduced by zinc dust and HOAc

Di benzyl derivative of the ethyl ether C_eH₂(OCH₂Ph)₂(CO Et)₂ [96 5°] Monoclinic needles (from alcohol), insol KOHAq

 $C_6H_2(OH)_2(CO NH OH)_{\bullet}$ Oxy-amide Formed by the action of hydroxylamine on the ether (Jeaurenaud, B 22, 1278) Prisms (containing 2aq), sol water and alcohol

Dioxyterephthalic acid dihydride CaHaO Succenyl succenic acid S 015 at 195° Got from its ether and the calculated quantity of cold NaOHAq Minute needles, decomposed by heat, yielding $C_eH_eO_2$ [78°] and CO_2 FeCl₃ colours its solution violet (Baeyer a Noyes, B 22, 2168) -BaA' 2 aq --(NH₄)₂A" 2aq

Methyl ether Me.A" [132°] Made by the action of sodium on methyl succinate (Ebert, A 229, 50) Got also from bromo acetoacetic ether and ammonia (Geuther, A 244, 204) Sol.

alcohol and ether

Mono ethyl ether EtHA" [98°] Got from the diethyl ether and cold NaOHAq (Herrmann) Yellowish prisms (from ether) Its alcoholic solution shows blue fluorescence FeCl. gives a violet colour Decomposed by boiling water into CO2 and CH,EtO4

Di-ethyl ether Et2A" i.e CO₂Et CH CO CH₂ CH CO₂Et or

CO Et CH CH COH) CH CO.Et [1270].

SG 19141 S (ether) 1 6 at 17°

Formation —1 By the action of K or Na on ethyl succinate (Fehling, A 49, 186, Herrmann, A 211, 306, Duisberg, B 16, 138).—2. By the action of NaOEt (free from alcohol) on succinic ether (Volhard, B 16, 134) -8 From bromo-acetoacetic ether by the action of alcoholic NH, (Duisberg, A. 213, 133) or of NaOEt (Wedel, A 219, 92) -4. By reducing di oxyterephthalic ether with zine and HClAq (Baeyer, B 19, 428)

Properties - Green triclinic crystals with blue fluorescence (from ether), v sl sol. hot water Insol NH,Aq, but forms a yellow solution in NaOHAq Its alcoholic solution shows blue fluorescence FeCl, gives a red colour Decomposed by excess of KOHAq, yielding black products containing syrupy ' succinyl-propionic' acid $C_1H_0O_4$ and a crystalline acid $C_2H_{10}O_6$ [139°], which forms BaA" 2aq The alkaline Does not solution is turned brown by oxygen react with phenyl cyanate (Goldschmidt a. Meissler, B 23, 258)

Reactions -1 Converted by bromine into di-oxy terephthalic ether Bromine and potash yield brominated quinones —2 Natrous acid forms a di nitroso-derivative C₁₂H₁₁N₂O₅ [114°], a white powder, insol water and alcohol, decomposed by boiling alcohol with formation of dioxy-terephthalic ether, and by boiling water with formation of the oxim of pyruvic ether -8 Hydroxylamine in presence of NaOHAq form C₈H₃(NOH), CO₂Et, crystallising from alcohol in plates which begin to decompose at 160° (Jeaurenaud, B 22, 1282) An alcoholic solution of phenyl-hydrazine forms the white hydrazo- com pound C.H. (NH NHPh)2(CO2Et)2 [165°] whence bromine produces the disazo compound $C_6H_4(N_2Ph)_2(CO_2Et)_2$ [126°], which on saponification yields the acid $C_6H_4(N_2Ph)_2(CO_2H)_2$ [over 250°] The white hydrazo- compound is accompanied by C₆H₄(NH NHPh)₂(CO₂Et)₂ [208°], a yellow isomeride identical with Knorr's body [206°] (Baeyer, B 24, 2690) —4 Phenyl hydrazine (2 mols) forms in presence of toluene and some glacial acetic acid, the four followsome glacial acetic acid, the four following compounds $C_0H_0O(N_1HPh)(CO_2Et)_2$ [160°], $C_0H_0O(N_1HPh)(CO_2Et)_2$ [206°], $C_0H_{12}N_1O_3$ [212°], and $C_0H_{11}N_1O_3$, decomposing above 800° (knorr a Bulow, B 17, 2054) The last body yields a di-methyl derivative $C_{12}H_{11}Me_2N_1O_2$ and is converted by introus acid into a blue substance $C_0H_1O(N_1)$ and $C_0H_1O(N_1)$ and $C_0H_1O(N_1)$ are the chlorides of di-C20H14N4O2-5 PCls forms the chlorides of dichloro dihydroterephthalic and dioxyterephthalic acids (Levy a Curchod, B 22, 2106)

Salts -Na,Et,C,H,O,2EtOH Got from the ether by ppg with alcoholic soda (Remsen, B 8, 1409) Red, on drying it changes to colourless Na Et C. H.O. (Hantzsch a Herrmann, B 21, 1756) Kc,H,O,Et, Colourless — K,Et,C,H,O, orange — MgEt,C,H,O, 2aq dark-red amorphous mass — BaC₁₂H₁₄O₆ aq red pp — CaC₁₂H₁₄O₆ aq

Di-acetyl derivative of the ether C.H.(OAc),(CO,Et), [171] Made from the ether and AcCl Needles (by sublimation) Its solutions are not fluorescent

Di-bensoyl derivative of the ether $H_4(OBz)_2(CO_2Et)_2$ [165°] Formed from C_eH₄(OBz)₂(CO₂Et)₂. [165°] Formed from C_eH₄(ONa)₂(CO₂Et)₂ and BzCl (Nef. A 258, 810) Formed also, together with two isomerides [1886] and [102 5°], by reducing the di-benzoyl derivative of di-oxy-terephthalic ether with zinc and HClAq The three isomerides may be separated by crystallisation from ether-ligroin. The three compounds are converted into C.H.(OH)2(CO2Et)2 by H₂SO, and into C₂H₂(OBz)₂(CO₂Et)₂ by Br in

(a)-Dr-bensyl derivative of the ether $C_cH_4(OCH_2Ph)_c(CO_cEt)_s$. [169°] Made in small quantity (5 pc) from $C_cH_2(OCH_2Ph)_c(CO_cEt)_s$ by reducing with Zn and HCI (Vef, A 258, 301) Colourless needles May be sublimed

(β)-D1-bensyl derivative of the ether C_cH₄(OCH₂Ph)₂(CO₂Et)₂ [148 5°] Made, to gether with a (γ)-isomeride [140 5°], by the action of benzyl chloride on C_cH₄(ONa)₂(CO₂Et)₂ at 100° Less sol alcohol than the (γ)-isomeride H₂SO₄ converts it into a crystalline polymeride

[272°] Hydroxylamine and phenyl hydrazine

have no action

Dr-ethyl derivative C.H. (OEt), (CO.H). [126 5°] Got, with EtBr, by heating bromoethyl acetoacetic ether at 100° (Wedel, A 219, 104) Trimetric octahedra, abc = 2451641Sol water and alcohol, forming acid solutions, coloured red by FeCl₁ — (NH₄)₂A" — Na₂A" 2aq — K₂A"aq — BaA" 2aq — CaA"aq — MgA" 2½aq — ZnA" 2½aq — MnA" 4aq — PbA" — Et₂A"

Di-oxy-terephthalic acid tetrahydride $C_{s}H_{10}O_{s}$ is $C_{s}H_{s}(OH)_{s}(CO_{2}H)_{2}$ [191°] by the action of hydroxylamine on dioxyterephthalic ether (Jeaurenaud, B 22, 1279) Prisms, sl sol cold water, v e sol alcohol and ether FeCl_a gives a brown colour —(NH₄)₂A" needles —BaA" white powder —Ag₂A" 2aq needles Ethyl ether Et₄A" [128°] Made by the

action of hydroxylamine on the hydrate of dioxyterephthalic ether [113°] (Hantzsch a Zeckendorf, B 20, 2801) Yekow crystalline body

Di-oxy-terephthalic acid hexahydride C_eH_s(OH)₂(CO₂H)₂ Dr oxy hexamethylene dr carboxylic acid The salt BaA''3 aq is got by saponifying the nitrile with baryta water (Baeyer a. Noyes, B 22, 2177) Thick prisms or needles, ▼ sl sol water

Nitrile C₆H₁₆O₂(CN), [180°] Made from quinone tetrahydride (diketohexamethylene) and HCy Colourless, v sol hot water and alcohol

c-D1-oxy-terephthalic acid [290°] $C_6H_2(OH)_2(CO_2H)_2[1\ 2\ 3\ 4]$ Formed from sodium pyrocatechin and CO_2 (Schmitt a Hahle, J pr [2] 44, 1) Thin needles (containing aq) forming solutions with deep blue fluorescence FeCl, gives a blue colour $-\mathrm{Na_2A''}$ 2aq fluor escent prisms $-\mathrm{Pb_1C_2H_2O_4}$ $-\mathrm{Ag_2A''}$ Methyl ether Me₂A'' [145°] Needles Ethyl ether Et₄A'' [90°] Tables

Tetra-oxy terephthalic acid acid C,H,O, Cs(OH)4(CO2H)2 Ethyl ether Et,A" [178°] Formed by passing SO, into a feebly alkaline solu tion of di-oxy-quinone dicarboxylic ether (Loewy, B 19, 2388) Golden plates (from chloroform), v sl sol water, alcohol, and ether In presence of NaOHAq it is oxidised by air to di-oxy-quinone dicarboxylic ether (Böniger, B 22, 1284) Phenyl cyanate (4 mols) and some chloroform at 170° yield C₆(O CO NHPh)₄(CO₂Et)₂[260°], an orange powder, insol most solvents (Goldschmidt a powder, insol most solvens (Columnia) with the tetra acetyl derivative C₄(OAc)₄(CO,Et)₂ [202°], a colourless crystalline powder (Hantzsch a. Zeckendorf, B 20, 2798) Hydroxylamine forms C₂O₃(O NH₃OH)₂(CO₂Et)₂ [170°] Alooholic phenyl-hydrazine forms, on boiling, the corre-sponding salt C₂O₂(O N₂H₄Ph)₂(CO₂Et)₂ [184°] (Böniger)

Reference - DI CHLOBO-DI-OXY-TEREPHTHALIC

DI OXY-TETRADECANE v BUTYBO PINACONE and DI ISOBUTYL-PINACONE

DI OXY-TETE ADECOIC ACID C₁₄H₂₀(OH),O₂ [60°] A product of exidation of oil of millet by KMnO₄ (Kassner Ar Ph [3] 25, 1081) Insol water, v sol alcohol and ether

OXYTETRIC ACID, formed by heating methyl acetoacetic ether with bromine and a little water, is identical with MESACONIC ACID (Cloez, Bl [3] 3, 598, C R 110, 583, Walden, B 24, 2033, Gorboff, J R 1887, 605)

a-OXY-THIENYL-ACETIC ACID

C.H.S CH(OH) CO.H [115°] Formed by reducing thienyl-glyoxylic acid with sodium amalgam (Ernst, B 19, 3280) Needles (from benzene), v sol water, alcohol, and ether Yields thiophenic aldehyde on boiling with MnO₂ Reduced by HI and P to thienyl acetic acid —BaA', xaq —CaA', xaq v sol water —Ag₂A" white pp

o-OXY THIOBENZOIC ACID C,H. SO, te C.H. (OH) CO SH Made from o-oxy benzoyl chloride and KSH (Carius, A 129, 11) Brownish yellow amorphous mass, insol water —BaA'2

Methyl derivative of the ethyl ether C_sH₄(OMe) CO SEt (198° at 80 mm) Made from C_sH₄(OMe) CO OPh and NaSEt in ether (Seifert, J pr [2] 31, 475) Oil, smelling like merciptan

o Oxy-thiobenzoic acid C_cH₄(OH) CS OH Amide C_cH₄(OH) CS NH₂ [118°] Made by fusing salicylamide with P₂S₃ (Spilker, B 22, 2767) Colourless needles, v soi alcohol FeCl₂ colours its aqueous solution violet Slowly converted into C_cH₄(OH) CO NH₂ by boiling water

Di oxy dithio benzoic acid C_eH₃(OH), CS,H. [421] Made by heating resorein with potassium xanthate at 100° (Lippmann, M 10, 618) Yellow needles (containing aq) Melts at 131° when hydrated, but decomposes at 124° when anhydrous Potash fusion yields (4,2,1)-di-oxybenzoic acid

Tri oxy di-thio-benzoic acid

C_zH_z(OH), CS_zH [4 3 2 1] [154°] Made by heating pyrogallol with potassium xanthate and alcohol (L) Yellow crystals (containing aq), w sol alcohol and ether Yields c-tri-oxy benzoic acid when fused with potash

OXY THIONAPHTHENE C.H.SO 1.6.

CH CH C C(OH) CH [72°] Made by heating throphenic aldehyde with sodium succinate and Ao₂O at 135° (Biedermann, B 19, 1618) Needles (by sublimation), sl sol water, v sol NaOHAq Gives the indophenine reaction Chloroform and KOHAq give a bluish-green colour on warming

OXY THYMOQUINONE C₁₆H₁₂O₂ i.e C₆HMe(C₅H₁)(OH)O₂ [1 4 6 2 5] [165°] Formation —1 By the oxidising action of

Formation—1 By the oxidising action of FeCl, on di-amido-thymol (Carstanjen, J pr [2] 15, 399, Ladenburg a Engelbrecht, B 10, 1218) 2 By dissolving bromo thymoquinone in KOHAq (Carstanjen, J pr [2] 3, 57)—3 By the action of H₂SO₄ or HClAq on methylamidothymoquinone (Zincke, B 14, 97) or dimethylamidothymoquinone (Schulz, B 16, 898)

Properties — Yellow needles, sol. alcohol, ether, and hot water Forms a violet red solution in alkalis May be sublimed

Reactions -1 EtI at 100° forms CieHiEtO

which sublimes in golden plates —2 Aniline in alcohol forms C₂Me(O₂H₂)(OH)O₂(NHPh) [185°], crystallising in violet-black needles, and forming a bluish violet solution in NH₂Aq —3 p-Tolu adme yields the corresponding p-toluide [165°]

(β) Oxy-thymoquinone
C_sHMe(C₃H,)(OH)O₂[1 4 3 2 5] [183°] Made
from di nitro carvacrol by reduction and subsequent oxidation with FeCl₂ (Mazzara, B 23,
1390) Orange prismatic tables, volatile with
steam Na₂CO₂Aq forms a violet solution

D1-oxy thymoquinone C_eMe(C₂H₁)(OH)₂O₂ [213°] Formed by boiling chloro-oxy thymoquinone with KOHAq (E a L) and by boiling dimethylamido thymoquinone with alcohol and H₂SO₄ or KOH (Zincke, B 14, 95) Red needles or prisms, forming a violet solution in alkalis Phenylene phenyl o diamine, in presence of alcohol and HOAc, forms oxythymophenindulone

 $C_aH_4 < N_{Ph} > C_aMe(C_3H_2)(OH)O$ as ruby-red crys tals [175°] (Kehrmann a Messinger, B 24, 590) —BaA" aq —PbA" green pp

Dr-acetyl derivative [81°] Needles Dr benzoyl derivative [163°] Reference — Chloro OXY THYMOQUINONE

DI OXY-DITHYMYL ETHANE C₂₂H₃₀O₂ 4.6 CH, CH(C₁₀H₁₂OH), [185°] Formed by reducing CCl₃ CH(C₁₀H₁₂OH), with zinc-dust and alcohol (Jager, C J 31, 262) and also by adding a mixture of chloroform and SnCl₄ to a cooled mixture of paraldehyde and thymol (Steiner, B 11, 287) Efflorescent plates (from alcohol)

Dracetyl derivative [100°] Needles Dr bensoyl derivative [191°] Needles Drethyl ether C.H.Et.O. [72°] DIOXY-DITHYMYL-ETRYLENE

CH₂ C($C_{10}H_1$, OH)₂ [171°] Formed, together with the preceding body, by boiling the compound CCl₃ CH($C_{10}H_{12}$ OH)₂ with zinc dust and alcohol (Jager, C J 31, 263) Needles (from HOAc) K₂FeCy₆ oxidises it, in alcoholic solution, to C₄,H₅,O₄ [215°], crystallising in green needles Alkaline K₂FeCy₆ forms $C_{22}H_{26}O_2$ [215°], which forms dark-red crystals

DI-OXY DI-THYMYL SULPHIDE (C₁₀H₁₂OH),S [152°] Formed from thymol and SCl₂ (Tassinari, G 17, 92) OXY-TOLUANIDOXIM

Formed from the thoamide in alcohol by treatment with hydroxylamine hydrochloride and NaOHAq (Goldbeck, B 24, 3662) Yellowish plates (from benzene), v sol hot water Coloured cherry red by FeCl,—B'HCl [215°]

Acetyl derivative Plates (from benzene).

Acetyl derivative Plates (from benzene) gives C,H_e(OH) C N O CMe [45°] on heat

ing with water in a sealed tube

Bensoyl derivative C,H₆(OH) C(NOB2) NH₂ [182°] Plates, sl sol alcohol Coloured green by FeCl, in acetone Di-bensoyl derivative [143°]

c-Oxy-toluamidoxim
[3 2 1] C,H,Me(OH) C(NOH) NH, [126 5°]
Formed from the nitrile and hydroxylamine
(Paschen, B 24, 3670) Tables, v sol alcohol
and hot water Yields a dibenzoyl derivative
C,H,Me(OBz) C(NOBz) NH₂[164°], whence KOH
forms C,H,Me(OH) NO CPh [150°]

OXY-TOLUENE v. CRESOL and BENZYL

Di-oxy-toluene C,H8O2 & e C.H.Me(OH)₂[1 2 4] Cresorcin Lutorcin Mol w 124 [104°] (c 269°) Formed from amido p cresol and from amido o cresol [161°] by the diazo reaction (Knecht, A 215, 92, B 15, 298, Wallach, B 15, 2835) Formed also by potashfusion from the corresponding toluened isulphonic acid (Nolting, B 19, 136) and from brome p-cresol (Vogt a Henninger, C R 94, 650) Spherical crystalline groups, v sol water, alco hol, and ether, sl sol benzene and ligroin FeCl₃ colours its solutions blue NH3 with damp air turns it brown, green, and finally blue Bleach ing powder gives a yellow colour Its solution in NaOHAq is turned brown by air On heating with chloroform and NaOHAq it gives a rose red colour On heating with phthalic anhydride it forms the phthalein $C_{22}H_{16}O_5$, which is a brick

nitro-benzene is diluted and made alkaline Dr acetyl derivative C, H, (OAc) [c 160°] D1-oxy-toluene C6H2Me(OH) [1 2 6] Made by the diazo reaction from amido cresol [124°-128°] (Ullmann, B 17, 1960)
Needles, v sol water and alcohol Coloured red
by bleaching powder With phthalic anhydride it gives a compound analogous to fluorescein Reduces cold ammoniacal AgNO.

red powder, exhibits green fluorescence in al kaline so ution, and yields C₂₂H₁₄Ac₂O₅ [260°]

Unlike resorcin, cresorcin gives no colour when

the product got by heating with H2SO4 and

Iso-orein $C_7H_6(OH)_2$ [87°] (260°) Made by potash fusion from toluene (γ) disulphonic acid (Senhofer, A 164, 131) Needles (contain-Sol water, alcohol, and ether sweet FeCl₃ gives a brownish green colour Reduces cold ammoniacal AgNO,

Other di-oxy-toluenes are described as Hy DROTOLUQUINONE, ISOHYDROTOLUQUINONE, ORCIN,

and METHYL PYROCATECHIN

ω-OXY-TOLUENE PHOSPHINIC ACID C₆H₅ CH(OH) P(OH)₂ [90°] Formed, together with (C₆H₅ CH(OH))₂PO OH [165°] by heating benzoic aldehyde with hypophosphorous acid (Ville, C R 107, 659, 110, 348) Plates, decom Reduces AgNO₃—Ba(HA")₂ ½aq small plates

Acetyl derivative CHPh(OAc) P(OH)₂

a OXY TOLUENE PHOSPHONIC ACID

 $C_6H_5 CH(OH) PO(OH)_2$ [173°] Made from benzoic acid by successive treatment with PCl. and water (Fossek, M 7, 34) Hard crusts (from benzene and HOAc) —BaA" —Ba(HA"), OXY-TOLUENE SULPHONIC ACID v

CRESOL SULPHONIC ACID

CaHaO OXY o - TOLUIC ACID C.H.Me(OH) CO.H[2 3 1] Oxy methyl-benzoic acid Mol w 152 [183°] Formed by the diazo- reaction from amido o toluic acid [191°] and by potash-fusion from sulpho o toluic acid (Jacobsen, B 16, 1963, 17, 163) Needles, sol cold water, alcohol, and ether, sl sol chloroform

Volatile with steam FeCl₃ gives a brown pp

Methyl derivative C₄H₃Me(OMe) CO₂H

[148°] Needles, sl sol cold water — CaA'₂ 2aq

Oxy-o-toluic acid C₆H₃Me(OH) CO₂H[2 4 1]

[179°] Formation — 1 By potash fusion from the corresponding aldehydo (Tiemann a Schot-

ten, B 11, 778), and from the corresponding

Properties - Needles (conta ning aq), v sol hot water, alcohol, and ether, insol cold chlord form Not coloured by $FeCl_3$ Yields m cresol on distillation — CaA'_2 2aq crystals, v sol water

sen, B 17, 164)

Methyl derivative C6H3Me(OMe) CO.H

 $C_0H_3Me(SO_2NH_2)CO_2H$ (Jacobsen, B 14, 40) -2 By heating m-cresol with CCl, and alcoholic NaOH (Schall, B 12, 819) -3 From amido-o toluic acid [c 165°] by the diazor reaction (Jacob

[176°] Needles (from water)

Oxy-o-toluic acid C₆H₃Me(OH) CO₂H[2 5 1] [172°] Formed by potash fusion from the corresponding C₆H₂Me(SO₂NH₂)CO₂H, and also from amido o toluic acid [196°] by the diazo reaction (Jacobsen, B 14, 41, 17, 163) Prisms Prisms, sol alcohol, ether, and hot water, v sl sol chloro Volatile with steam FeCl, gives a brown form Volatile with steam possible of the Cu salt forms bluish green plates

Oxy o-toluic acid C_sH₃Me(OH) CO₂H[2 6 1] 8°] S 143 at 25° Formed by potashfusion from brome o toluic acid (Jacobsen, B 16, 1962) Long needles, v sol hot water, alco Volatile with steam At 200° it hol, and ether yields m cresol FeCl_2 gives a bluish violet colour

Oxy-m-tolunc acid C₂H₃Me(OH) CO H[3 2 1] Homosalicylic acid (3) Cresotic acid [164°] Formation -1 By the action of CO, on sodium o cresol (Engelhardt a Latschinoff, Z 1869, 623, Kekulé, B 7, 1006, Ihle, J pr [2] 14, 456) —2 By heating o cresol with CCl, and NaOH at 100° (Schall, B 12, 8 6) —3 By means of potash fusion from the corresponding $C_6H_3Me(SO_2NH_2)CO_2H$ (Jacobsen, B 11, 902) -4 From c amido toluic acid (Jacobsen, B 14, 2354)

Properties —Long needles, sl sol cold water, v sol chloroform Volatile with steam FeCl. gives a violet colour Poisonous (Dunstan a

Black, Ph [3] 21, 429)

Methyl derivative
[81°] Feathery needles C,H6(OMe) CO2H

Methyl ether MeA' (235°) SG 1 1444 (Pinner, B 23, 2938)

Ethyl ether Eth' (248°) SG 23 1 1020 With benzamidine it forms C2H1, NO crystal lising in yellowish needles, insol acids and alkalis (Pinner, B 23, 2939)

Natrale C,H6(OH) CN [88 5°] Got from its acetyl derivative, which is formed by the action of Ac_2O on the oxim of c toluic aldehyde (Paschen, B 24, 3669) Tables, v sol alcohol

Oxy m toluc acid C₂H₃Me(OH)CO,H[3 4 1] [173°] Formation—1 By potash fusion from the corresponding C₂H₃Me(SO₂NH₂)CO₂H (Jacobsen, B 11, 897, Remsen a Iles, Am 1, 87, B 11, 462, Mahon, Am 4, 186), from bromo m-toluic acid and from chloro m-toluic acid [210°] (Jacob sen, B 14, 2351, 18, 1761)—2 By heating o cresol with CCl, and NaOH, the yield being 40 pc (Schall, B 12, 816)—3 By the diazo reaction from amido m toluic acid (Remsen a Kuhara, Am 3, 428) -4 By oxidation of the corresponding aldehyde (Tiemann a Schotten, B 11, 777)

Properties -Long needles (containing aq) sol hot water, alcohol, and ether, insol cold chloroform Gives no colour with FeCl. Yields o cresol when heated with HClAq at 180° Gives

a nitro- compound [85°].

Salts — CaA', 3aq minute needles — BaA', 3aq.—CuA', 21aq blue flocculent pp Methyl derivative C.H.Me(OMe) CO,H [198°] Minute needles Got by saponifying C.H.Me(OMe) CO Me [67°] (Schall) The amide C.H.Me(OMe) CONH. [144°] is prepared from C.H.Me(OMe) [1], ClCONH., and AlCl. (Gatter main, A 244, 64]

Ethyl derivative C.H.M. (ON)

Ethyl derivative C.H.Me(OEt) CO.H [199°] Obtained by saponification of the amide

C,H,Me(OEt) CONH₂ [167°] which is got from C₈H,Me(OEt) and ClCONH₂ (G)—CaA'₂2aq (Brown, Am 4, 375)

s Oxy m toluic acid

CaH3M°(OH) CO2H [3 5 1] $[208^{\circ}]$ Formed from m toluic acid by sulphonation followed by potash fusion, the resulting acid being freed from its isomeride by steam distillation (Jacobsen, B 14, 2357) Formed also by the action of baryta water on $C_{12}H_{16}O_8$ [90°], which is obtained from acetyl pyruvic ether and NaOHAq (Claisen, B 22, 3271) Needles or prisms, v sol hot water, not volatile with steam - CaA', 2aq prisms -SrA'2

Methyl ether MeA' [93°] Needles.

Oxy m toluic acid

C₆H₃Me(OH) CO₂H[3 6 1] p-Homosalucyluc acad

(a) Creosotic acid [151°]

Formation -1 By passing CO₂ over p cresol in which sodium has been dissolved (Engelhardt a La'schnoff, Z 1869, 622, 712, Kolbe a Lautemann, A 115, 203, Ihle, J pr [2] 14, 455)

2 By heating p cresc' with CCl, and NaOH (Schall, B 12, 816) — 3 By potash fusion from chloro m xylene sulphonic acid (Voigt, Z [2] 5, 577, B 2, 284), from m xylene sulphonic acid (E a L), from (1,3,4) xylenol or its (β) sulphonic acid, from bromo m toluic acid, and from sulphom toluic acid (Jacobsen, B 11, 374, 14, 2352, Staedel a Holz, B 18, 2919) -4 By oxidation of the corresponding aldehyde (Tiemann a Schotten, B 11, 778) -5 From amido toluic acid [172°] by the diazo reaction (Panaotovic, J pr [2] 33, 64)

Properties - Colourless trimetric (from water), sl sol water, v sol alcohol, ether, Volatile with steam Its and chloroform aqueous solution is turned violet by FeCi, Conc HClAq at 180° yields p cresol POCl,, forming various dehydration products (Schiff, A 245, 43) Distillation with Aco yields C15H12O2

[143°] (Kostanecki, B 18, 1988)

Salt — BaA', 2aq leaflets

Methyl ether MeA' (242°)

1 1438 Liquid (Pinner, B 23, 2938)

Ethyl ether EtA' (251°) S G

1 1037 Reacts with benzamidine, forming C₂₂H₁₇N₈O crystallising in yellowish needles (P)

Ameas C.H.Me(OH) CONH₂ [178°] Got from the acid by treatment with POCl₂ at 60° rom the acid by treatment with POCi, at 60° followed by alcoholic NH_s at 160° (Schiff, G 17, 559, A 245, 43), and from the ether and NH_s (Goldbeck, B 24, 3659) Needles (from alcohol) P₂C₅ forms C,H_s(OH) CS NH_s [127°] Antitade O,H_s(OH) CONHPh [53°] Plates N*tr*le* C,H_s(OH) CN V sol alcohol Its acetyl denvative [57°] is got by the action of Ac.O on the oxim of toluce aldebyde.

Ac₂O on the oxim of toluic aldehyde

Methyl derivative C.H.Me(OMe) CO.H. [70°] (L), [67°] (Schall, B 22, 749) Long needles -AgA'

Amide of the methyl derivative C_eH₄Me(OMe) CONH₂ [163°] Made from C_eH₄Me(OMe) and ClCONH₂ in presence of AlCl

(Gattermann, A 244, 66) Needles (from hot Aq)
Nitrile of the methyl derivative
C_sH₂Me(OMe) CN (270° uncor) Made by warming diazotised amido p cresol with CuCy,

(Limpach, B 22, 351) Oil

οf the ethyl Amide derivative C_aH_•Me(OEt) CONH C₆H₃Me(OEt) CONH [152°] Made from C₆H₄Me(OEt), ClCONH₂, and AlCl₃ (G) Silky

needles (from dilute alcohol)

Oxy p toluic acid C_eH₂Me(OH) CO₂H [4 2 1]. (γ) Cresotic acid m-Homosalicylic acid [177° cor] Formation -1 By passing CO₂ into m cresol in which sodium has been dissolved (E a L, Biedermann a Pike, B 6, 323) -2 By oxidation of the corresponding aldehyde (Tiemann a Schotten, B 11, 777) —3 By heating m cresol with CCl, and NaOHAq (Schall, B 12, 816) -3 By potash fusion from p xylenol (Jacobsen, B 11, 570)

Properties - Needles (from water) or mono clinic prisms (from alcohol), m sol hot water, v sol alcohol and chloroform Volatile with steam FeCl_s gives a red colour HClAq at

170° yields m cresol

Salts — CaA'. 3aq — BaA'. 3aq prisms Methyl ether MeA' (243°) S G 23 1 1395 (Pinner, B 23, 2938)

Ethyl ether EtA' (254°) SG 23 1 0973 Converted by benzamidine into CzH1, N3O crystallising in needles [235°]

Methyl derivative C₆H₃Me(OMe) CO₂H [104°] Leaflets, sol hot water (Schall)

Ethyl derivative C.H.Me(OEt) CO2H [109°] Got by oxidising the ethyl derivative of thymol (Paterno, J 1879, 519)

Oxy p toluic acid C.H.Me(OH) CO2H [4 3 1] [207° cor]

Formation -1 By potash fusion from sul pho p toluic acid or its mono amide (Flesh, B 6, 481, Remsen a Hall, Am 2,54, Weinreich, B 20, 981), and from chloro or bromo p toluic acid (Gerichten, B 11, 368) —2 From nitrotoluic acid [190°] by reduction, followed by the diazo reaction (Fittica, B 7, 927)

Properties - Needles, sol hot water, alcohol, and ether, insol chloroform Volatile with Not coloured by FeCl, Gives o cresol steam

on distillation with lime

Salts — CaA', 4aq — PbA', 2aq needles Ethyl ether EtA' [75°] Prisms

Methyl derivative C.H.Me(OMe) CO.H.

[156°] Needles (by sublimation) —BaA', 4aq ω Oxy o toluic acid CH₂(OH) C₆H, CO₂H [118°] Made by dissolving phthalide in boiling NaOHAq (Hessert, B 10, 1446, 11, 237) Powder, v sl sol cold water, v sol alcohol and ether Changes on fusion, and on boiling with water, into its anhydride -BaA'2 -AgA' octahedra

Anhydride v Phthalide

ω-Oxy p toluic acid CH₂(OH) C₆H₄ CO₂H.
Oxymethyl-benzoic acid [181°] Formed, together with terephthalic acid and C.H. (CH2.OH), by boiling terephthalic aldehyde with NaOHAq (Löw, A 231, 373) Formed also by boiling CH2Br C.H. (CO,H with baryta-water (Kekulá a. Ditmar, A 162, 342) Plates or needles, v sol. water and ether Not reddened or resimined by H₂SO₄ -AgA'

Di-oxy-o-toluic acid C_eH₂Me(OH)₂CO₂H | [2 5 8 1] Cresorsellic acid Mol. w 168 [445°] 8 86 at 0° Formed by fusing di sulpho o-toluic acid with potash (Jacobsen, B. 16, 1960) Long FeCl. needles, v sol alcohol and boiling water gives a brownish-black colour Reduces alkaline Ag and Cu solutions Conc H2SO4 gives a bright red colour on heating -NH, A' 2aq prisms

Di oxy-toluic acid Methyl derivative C.H.Me(OMe)(OH) CO2H[1345] Creosol carb-[1826] Obtained by the action of oxylic acid CO₂ upon sodium creosol (Wende, B 19, 2324) Concentric needles Sublimable V sol alcohol, ether, and chloroform, sl sol water, nearly insol benzene Gives a blue colouration with FeCl,

Salts - NH,A' needles - KA' small readily soluble needles —BaA'₂ small needles —PbA'₂ white pp —CuA'₂ yellow powder Methyl ether MeA' [92°], small colour-

less trimetric crystals, abc = 5285 1 07334

Gives a bluish green colour with FeCl

Ethyl ether EtA' [77°], small needles Di oxy-m toluic acid C₆H₂Me(OH)₂CO₂H [1 2 4 dor5] Cresorein carboxylic acid [208°] Made by boiling cresorein (di oxy toluene) (1 pt) with NaHCO, (4 pts) and water (8 pts) (Kosta necki, B 18, 3203) Prisms (containing aq), v e sol water - KA' 2aq prisms, v sol water

D1 oxy p toluic acid $C_6H_2Me(OH)_2CO_2H$ [4531] [176°] Formed by heating disulpho p toluic acid with KOH (Weinreich, B 20, 981) Needles, v sol water, alcohol, and ether

D1 - oxy - toluic acid C6H2Me(OH)2CO2H Hydrotoluquinone carboxylic acid [206°-210°] S 07 at 8° Formed by heating hydrotoluquinone with KHCO, and conc K.SO, Aq at 160° (Brunner, M 2, 458) Trimetric plates (from alcohol) or indistinct crystals (containing 1 aq) (from water), m sol hot water and alcohol FeCl₃ gives a blue colour Reduces ammoniacal AgNOs in the cold Yields hydrotoluquinone on fusing Conc H₂SO, at 160° yields tetra oxy di methyl anthraquinone, a dark red powder -

CaA'₂ 2aq —BaA'₂ 2aq —PbA'₂ 2aq crystalline Ethyl ether EtA' [98°] Needles

Di oxy p-toluo acid C.H.Me(OH),CO,H Orsellic acid Orsellinic acid Orsellesic acid [176°] S (ether) 22 at 20° Formed by boil ing lecanoric acid or erythrin with lime water, baryta water, or NaOHAq (Stenhouse, P M [3] 82, 300, Pr 12, 263, A 68, 61, Hesse, A 117, 312, 139, 35) Prisms (containing aq), v e sol alcohol, sol water Splits up on fusion, or on boiling with water, into CO_2 and orcin FeCl₂ gives a purple colour Bromine gives tri bromo orcin POCl, acting on the anhydrous acid at 90° forms a blue liquid which, when poured into water, ppts C40H30P4O24, a blue substance with coppery lustre resembling indigo The solutions of this 'phosphorsellic acid' in water and alco hol are intensely blue, and it is ppd from aqueous not are intensety due, and it is ppu from aqueous solution by HCl, by H₂SO₄, and by NaCl Phosphorsellic acid forms C₄₀H₂₂Pb₇P,O₂₄ and C₄₆H₂₄Pb₁₁P₄O₂₄, an anilde C₄₆H₂₄(NHPh)₂P₄O₂₂ which gives C₂₆H₂₆Pb₉(NHPh)₄P₈O₄₄, and an acetyl derivative C₄₆H₂₅Ao₂P₄O₂₄ as a dark violet mass which gives C₄₆H₂₆(PbOH)₈Ao₂P₄O₂₄ (Schiff, A OGC E2) 4 228, 56)

Salt -Ba(C,H,O,), xaq prisms Methyl ether MeA' Made

lecanoric acid or erythrin with MeOH Silky needles (from boiling water)

Ethyl ether EtA' [182°] Got in like manner (Heeren, Schw J 59, 341, Liebig, P 21, 32, Kane, Tr 1840, 287, 279, Schunck, A 41, 160, 61, 72, Rochleder a' Heldt, A 48, 5, Stenhouse, C J 20, 224, Strecker, A 68, 111, Hesse, A 117, 297) May be prepared by repeatedly exhausting Roccella tinctoria with boiling alcohol and evaporating the extract Thin needles, nearly insol cold water, v sol alcohol and alkalis Yields C₆Cl₂Me(OH)₂CO₂Et [162°] on chlorination

Isoamyl ether C.H.A' [76°] Prisms Di oxy-o-toluic acid C.H.Me(OH),CO.H Paraorsellic acid [172°] [6 4 2 1] ນ 17 m Formed by heating orcin with a soluthe cold tion of ammonium carbonate, KHCO, or NaHCO, (Senhofer a Brunner, M 1, 236, Bistrzycki a Kostanecki, B 18, 1986), or by heating potassium orcin in a current of CO, at 250° (Schwarz, B 13, 1643) Needles (containing aq), sl sol water, v sol alcohol and ether FeCl, gives a blue colour Boiling water decomposes it into CO₂ and orcin POCl₃ followed by water gives $P_2(C_8H_8O_4)_3$, a chrome-green powder (Schiff, A 228, 56) -KA' $-BaA'_26aq$ $-Ba_3(C_8H_8O_4)_28aq$ -CuA', 4aq -AgA' nearly insol water

Di oxy-m-toluic acid CH, (OH) C, H, (OH) CO, H[3 2 1] [142°] Formed by reduction of aldehydo o-oxy-benzoic acid with sodium-amalgam (Reimer, B 11, 792) Prisms, v sol water, alcohol, and ether FeCl, gives a violet colour H,SO, gives a red colour Boil

ing HClAq resinifies it

Di oxy m-toluic acid $CH_2(OH) C_6H_3(OH) CO_2H[5\ 2\ 1]$ [above 270°] Formed by reduction of aldehydo p oxy benzoic acid (R) White powder, sl sol water Not coloured by FeCl, or by H,SO.

Di oxy m toluic acid CH₂(OH) C₆H₃(OH) CO₂H[3 6 1] Made by re ducing aldehydo o oxy benzoic acid (R) Prisms (from ether), sl sol water, m sol alcohol and ether FeCl, gives a violet colour Oxidised by KMnO, to oxy isophthalic acid, and by aqueous K2Cr2O, to aldehydo oxy benzoic acid

References -DI BROMO OXY-TOLUIC ACID and

DI-10DO-ORSELLIC ACID

ALDEHYDE C.H.O. 1e 41] [110°] Prepared, OXY-0 TOLUIC C_eH_sMe(OH) CHO[2 4 1] Prepared, together with the (4,2,1) isomeride, by heating m cresol with chloroform and NaOHAq (Tie mann a Schotten, B 11, 773) Flat leaflets (from water), not volatile with steam FeCl, gives a red colour

Phenyl hydrazide C_sH_sMe(OH) CH N_sHPh [151°] (Paschen, B

24, 3671)

Oxy m toluc aldehyde C.H.Me(OH) CHO 4 1] [115°] Formed, together with the (3,2,1) isomeride, by the action of chloroform and potash on o cresol (Tiemann a Schotten, B11, 772) Long prisms (from water), not volatile with steam FeCl, gives a bluish violet colour

Yields a nitro-derivative [152°]

Acetyl derivative O.H. (OAc) CHO [40°]
(275°) Needles (Staats, B 13, 138, Barbier,

Bl [2] 88, 52, C R 90, 87).
Oxy-m-toluic aldehyde C,H,Me(OH) CHO Made by boiling [8 2:1] [17°] (209°) Formed as above (T a. S). Crystals, volatile with steam FeCl, gives a bluish colour Forms a yellow solution in NH, Aq

Acetyl derivative C₁₀H₁₀O₃ (267°) (B). Oxim. [99°] (Paschen, B 24, 3668)
Phenyl hyd aside [95°] Tables
Oxy-m-toluic aldehyde C.H.Me(OH) CHO

(218°) Formed by the action [56°] c! CHCl, and KCH on p cresol (T a S) White leaflets FeCl, gives a green colour Yields a nitro- derivative [141°]

Acetyl derivative C.H.Me(OAc) CHO Long needles Made by the action of Ac,O on the ethereal solution of the K salt Combines with NaHSO, With Ac₂O it unites in the cold, forming C₆H₃Me(OAc) CH(OAc)₂, which crystallises in prisms [94°] and does not

combine with NaHSO,

Methyl derivative C.H.Me(OMe) CHO (254°) Colourless liquid

Oxim C₆H₃Me(OH) CH NOH. Needles (Goldbeck, B 24, 3658) [105°]

Oxy-p-toluic aldehyde C.H.Me(OH) CHO [4 2 1] [54°] (223°) Made, together with the (2,4,1)-isomeride, by the action of chloroform and potash on m-cresol (T a S) Crystals, volatile with steam FeCl, gives a violet colour

Di oxy o-toluic aldehyde C.H.Me(OH),CHO [6 4 2 1] Orcyl aldehyde [178°] Formed by heating orcin with chloroform and potash (Tie mann a Helkenberg, B 12, 999), and also by potash-fusion from methyl umbelliferone (Pechmann a Welsh, B 17, 1646) Needles, sol alcohol and hot water FeCl, gives a reddish-Aniline forms the compound brown colour C₆H₂Me(OH)₂CH NPh [126°], crystallising in yellow prisms

Di oxy m-toluic aldehyde Methyl dersvative C, H, Me(OH)(OMe)CHO [5 2 3 1] (270°-275°) Formed by the action of chloroform and NaOHAq upon creosol (Tiemann a Koppe, B 14, 2026) Oil, sol alcohol FeCl, colouis its

alcoholic solution green

OXY-TOLUIDINE v Amido cresol

OXY-TOLUQUINOLINE v OXY-METHYL-

DI-OXY-TOLUQUINONE C₆HMe(OH)₂O₂. [177°] Made by digesting oxy phenylamido-toluquinone amilide with dilute KOHAq (Hagen a Zincke, B 16, 1562) Brownish yellow plates, v sol most solvents May be sublimed

Tri-oxy toluquinone CoMe(OH),O2 Formed from tri amido-orcin by treatment with FeCl., the resulting amido diimido-orcin being heated with HClAq at 150° (Merz a Zetter, B 12, 2044) Dark crystals, nearly insol cold alcohol Yields a crystalline tri acetyl derivative

Reference -- DI-BROMO- and DI CHLORO- OXY-TOLUQUINONE

OXY-"OLUQUINOXALINE

 $\begin{bmatrix} 1_4^8 \end{bmatrix} C_e H_e Me <_N^N \stackrel{CO}{OH} H$ [267°] Formed by oxidation of its dihydride [c 127°], which is got by condensing tolylene diamine with chloroacetic ether (Hinsberg, B 18, 2870, A 248, 75), or by reducing nitro-tolyl amido acetic acid (Plochl, B 19, 6) Yields a methyl derivative [71°], and an ethyl derivative [67°]

Isomeride v OXY METHYL-QUINOXALINE

NCOH $C_nH_nMe < \tilde{N} \ \tilde{C} \ \tilde{O}H$ Di-oxy-toluquinoxaline [above 800°] Formed by heating tolylene-c Formed from o amido benzyl alcohol and allyl

diamine with oxalic acid at 150° (Hinsberg, B. 15, 2690, A 237, 348) by reducing natro-tolyloxamic acid, and by heating tolylene-diamine dicyanide with HClAq at 150° (Bladin, B 18, 670) Needles—NaHA"—Ag₂A".—H₂A" HOAc. Plates.

DI-OXY-DITOLYL

[3 4 1] C.H.Me(OH) C.H.Me(OH) [1 8 4] o-Dicresol [157°] (H), [161°] (G) Made from di amido-ditolyl by the diazo- reaction (Gerber, B 21, 749, Hobbs, B 21, 1067) Needles, sl sol hot water, v sol alcohol and ether a di nitro derivative [273°]

Di-acetylderivative C₁₄H₁₂(OAc), [131°] Di benzoyl derivative [185°] Needles Di-ethyl ether C14H12(OEt)2. [156°] Made, together with ditolyl, by the action of alcohol on dı amıdo-dıtolyl (Schultz, B 17, 468)

plates, sol hot alcohol

Di-isoamyl ether [699] Leaflets. [69°]

Tetra-oxy-ditolyl C, H, O, & e

[1 2 5 6]C,H_Me(OH),C,H_Me(OH),[6 1 2 5] [202° uncor] Formed by oxidising hydrotolu-quinone, dissolved in HOAc with MnO₂ and H₂SO₄ in the cold (Brunner, M 10, 174) FeCl, oxidises it to the quinhydrone C. H.O., crystallising in violet scales [220° uncor], and finally to the quinone C₁₄H₁₀O₄ [163°], crystallising in yellow prisms

Tetra acetyl derivative

C14H10(OAc), [135°] Made by heating with NaOAc and Ac2O at 160° Needles

Anhydride C12H, Me2(OH)2O [232°] Got by heating C₁₂H₄Me₂(OMe)₂O₂ with HClAq at 180° (Nietzki, B 11, 1281) Colourless plates

(containing aq) (from dilute alcohol)

Di-methyl ether C12H4Me2(OMe)2(OH)2 [173°] Formed by partial methylation Colour-less needles, quickly oxidised in alcoholic solu-Yields a di acetyl derivative tion by air C₁₂H₄(Me(OMe)(OAc)[6 1 2 5])₂, crystallising in needles [123°] (Noelting a Werner, B 23, 3248)

Dehydride of the di-methyl ether C₁₄H₁₄O₄ i.e. C₁₂H₄Me₂(OMe) O₂. [153°] Formed by oxidation of the di methyl ether of hydrotoluquinone by chromic acid mixture (Nietzki, A 215, 161) Dark-red needles (from alcohol)

Tetra-methylether C₁₄H₁₀(OMe), [129°]

Di-ethylether C₁₄H₁₀(OEt), (OH), [138°]

Formed by the action of alcoholic ammonium sulphide on the dehydride (or quinone) $C_{1,}H_{16}(OEt),O_{2}$, which crystallises in green-black needles [139°], and is made by oxidising $C_{s}H_{s}Me(OEt)_{z}$ with chromic acid mixture (Noelt-

ing, B 23, 3247, Bl [3] 4, 805) White needles a-OXY m-TOLYL-ACETIC ACID $C_0H_{10}O_3$ 1 ε m-Methyl man-[1 3]C_sH_sMe CH(OH) CO₂H delic acid [84°] Formed from m-toluic aldehyde, KCy, and HCl (Bornemann, B 17, 1469) Small plates (from benzene), v sol water

a-Oxy-p-tolyl-acetic acid
[1 4]C₆H₄Me.CH(OH) CO₂H₂ [146°] Made by reduction of p-tolyl-glyoxylic acid by zinc dust and ammonia (Claus a. Kroseberg, B 20, 2050) Tables (from water) — NaA' — KA' aq — CaA', –Ba**A', ∤a**q

Ethyl ether EtA' [77°] Need a-OXYTOLYL-ALLYL-THIO-UREA Needles. [1 2]C,H,(CH,OH) NH CS NH C,H,

thiocarbimide in benzene Oil, changed by warming with HClAq to C.H. CH. NC.H. [91°] Converted by HgO in alcohol to oxy allylquinazoline dihydride C,H, CH, NO,H, which crystallises in four sided prisms [78°], and yields B'H.PtCl. [171°] (Söderbaum a. Widmann, B 22, 1670, 2937)

OXY-TOLYL-BENZYLIDENE-TOLYLENE-

DIAMINE C21H20N2O 1 e

C,H, NH C,H, N CH C,H, OH [160°] Made from o-amido di p tolyl amine and salicylic alde hyde (O Fischer a Sieder, B 23, 3801) crystals, sl sol water, v sol benzene

OXY-p-TOLYL BENZYL-METHYL-PYK $C_eH_4Me\ C{\gtrless}_N^N\ C(OH){\lessgtr}C\ CH.Ph$ IMIDINE Made from p tolenyl amidine hydrochloride and benzyl aceto acetic ether (Pinner, B. 23, 3826) Slender needles (from pyridine), ınsol water, v sl sol hot alcohol

OXY-TOLYL CARBINOL

C₆H₂Me(OH) CH₂OH[5 2 1] [105°] Made by reduction of (2,5,1) oxytoluic aldehyde with sodium amalgam (Schotien, B 11, 784) Colourless leaflets

TRI-OXY TRI TOLYL CARBINOL Anhydride O₂₂H₄₀O₃ ie (C₆H₃Me(OH)) C CO Cresaurin Formed by heating p cresol with formic acid and ZnCl₂ at 110° (Nencki, J pr [2] 25, 275) Red amorphous powder, insol water, v

sol HOAc Forms a crimson solution in alkalis DI-OXY-DITOLYL DICARBOXYLIC ACID C₁₆H₁₄O₆ Made by heating sodium di oxy ditolyl with CO₂ in a closed vessel at 160° (Deninger, B 21, 1639) Crystals, insol water, sl sol alcohol and ether Not melted at 290° FeCl, gives a blue colour Yields a di acetyl derivative C ₀H₁₈O₈ [163°]

OXY-TOLYL-CROTONIC ACID Anhydride

v DI METHYL COUMARIN

Di oxy-tolyl crotonic acid Anhydride $C_6H_2Me(OH)$ < $CMe CH \\ O--CO$ Di methyl umbelli ferone [250°] Made by the action of H,SO, on a mixture of acetoacetic ether and orcin (Pech mann a. Cohen, B 17, 2188) Needles (from alcohol), nearly insol water On boiling with NaHSO 1t forms a solution coloured red by FeCl. [195°] Acetyl derivative CuH, AcO.

Needles, v sol alcohol
TRI OXY-TRI-TOLYL ETHANE CaHaMe(OH) CH2 CH(CaHaMe OH) isomerides with this formula are got by warming di-chloro-ethyl ether with o , m , and p- cresol respectively (Brückner, A 257, 322) They are amorphous powders, v sol alcohol and ether, insol water, and yield tri acetyl derivatives which are oxidised by FeCl, to anhydrides [C.H.Me(OH) CH.C(C.H.Me(OH))]2]2O
OXY-TOLYL-HYDRAZINE Methyl derr-

vative [148] C_eH₂Me(OMe) NH NH₂ [45°] Got from the methyl ether of amido p cresol by treatment with nitrous acid and subsequent re-

duction (Limpach, B 22, 351) Orystalline
Oxy-om-di-tolyl-hydrazine Ethyl derivatave [2 1]C,H,Me NH NH C,H,Me(OEt)[1 3 4] [78°]. Made by reducing the azo- compound

with alcoholic ammonium sulphide (Noelting a Werner, B 23, 3260, Bl [2] 4, 796) crystals, insol water, sol alcohol

The isomerides (2 1]C,H,Me NH NH O,H,Me(OEt)[1 5 2] [138°], [4 1]C,H,Me NH NH C,H,Me(OEt)[1 3 4] [°7°], [4 1]C_aH,Me NH NH C₆l ,Me(OEt)[1 5 2] [153°] are formed in like manner

DI 6XY-DI TOLYL KETONE C₁₅H₁₄O₅ te C₆H₃Me(OH) CO C₆H₃Me(OH) [138°] Got by potash-fusion from o cresol benzein, which is a product of the action of benzotrichloride on o cresol (Schroeter, A 257, 74) Colourless needles, v sol alcohol and ether

Di oxy di tolyl ketone CO(C₆H₃Me OH)₂ [104°] Made from p cresol phthalein C₂ H₁₈O₃ by potash fusion (Drewson, A 212, 341) Yellow needles (from alcohol), insol water, v sol alkalıs

OXY p TOLYL METHYL ETHYL PYRIM IDINEC, H, Me C N CMe SCEt [218°] Made from p tolenyl amidine and ethyl acetoacetic ether (Pinner, B 23, 3826) Hair like needles, m sol hot alcohol

OXY-TOLYL METHYL KETONE C, H,OQ 1 e [1 2 5]C₈H₃Me(OH) CO CH₃ [104°] from amido m tolýl methyl ketone by the diazo reaction (Klingel, B 18, 2699) Flat white prisms, v sol alcohol and hot water FeCl, gives a yellowish brown colour

Di oxy tolyl methyl ketone C₆H Me(OH) CO CH, [146°] Made from orcin, HOAc, and POCl₂ (Rasinsky, J pr [2] 26, 59) Needles, v sol alcohol, ether, and HOAc FeCl, colours its aqueous solution black

OXY o TOLYL METHYL PYRAZOLE

 $C_{11}H_1 N_2O$ se $C_0H_4Me N < CO CH_{N=CMe}$ Formed by heating o tolyl hydrazine with aceto acetic ether at 140° (knorr, B 17, 549) Colour less crystals With KOH and MeI it yields C,,H,, NeN,O [97°]

Oxy p tolyl methyl pyrazole $C_{11}H_1 \times O$ From p tolyl hydrazine and acetoacetic ether (K) Yields a methyl derivative [137°] The compound C,H, N CO C N NHC,H, [217°]

is formed, together with C2H22N4O2 by heating p tolyl hydrazine with thio acetoacetic ether (Buchka a Sprague, B 22, 2555, C J 59, 340)

OXY TOLYL METHYL PYRIMIDINE

 $C_{e}H_{4}Me \ C \underset{N}{\overset{N}{<}} \overset{CMe}{C(OH)} \searrow CH \quad [216^{\circ}] \quad Made \ from \quad$ tolenyl amidine and acetoacetic ether (Glock, B 21, 2658) Long white needles, m sol hot alcohol — Salts $B'_2H_2PtCl_2$ 2aq [241°] — $B'_2H_2Cr_2O_7$ 7aq [c 170°] Yellow plates — $B'_{2}H_{2}Cr_{2}O_{7}7aq$ [c 170°] Yellow $B'C_{6}H_{3}N_{3}O_{7}$ [196°] Yellow needles

β OXY TOLYL-DIPHENYL-ETHYLIDENE-AMINE C,H,N CPh CHPh OH [141°] Made by heating benzoin with o toluidine at 150° (Bandrovski, M 9, 693) Canary yellow needles

OXY-TOLYL-PROPIONIC ACID C10H12O2 8.6 CH, C(C,H,)(OH) CO,H Got from di bromo oxy tolyl-propionic acid CHBr, C(C,H,)(OH) CO,H by reducing with sodium amalgam (Bottinger, B 14, 1598) Long four sided tables, v sol

OXY-DI p-TOLYL PYRAZINE Tetra- $O_oH_aMe N < CH_aCO > N O_oH_aMe$ Ludride 'Ditolylmonoacipperasine' [168 5°] from p-toluidine by successive treatment with ethylene bromide and a mixture of chloro-acetic poid and NaO/Io (Bischoff, B 22, 1785, 28, Crystals, v sol water and ether

Di-oxy-di-o-tolyl-pyrazine Dihydride $C_eH_4Me N < CO_{CO}^{OH_2 \cdot CH_2} N C_eH_4Me$ acupiperazine [184°] Formed from di-o tolylethylene - diamine and oxalic acid at 200° (Bischoff, B 22, 1805, 23, 2034)

Di bxy di-p tolyl pyrazine dihydride [263°] Made by dissolving oxy di-p tolyl pyrazine tetrahydride in HOAc and oxidising with nitrous or chromic acid (B) Colourless plates, v sol. aniline and alcohol, sl sol ether and hot water. Alcoholic potash yields di tolyl ethylene-diamine [97°] and oxalic acid

Di oxy s di o tolyl pyrazine Dihydride $C_eH_iMe N < CO_{CH_2}CO > N C_eH_iMe$ [1609]

Formed by heating o tolyl-amido acetic acid at 220° (Bischoff a Nastvogel, B 22, 1787) and by the action of potash on the product of the action of chloro acetyl chloride on o toluidine (Widman, J pr [2] 38, 299, 305) Rectangular plates (from alcohol), insol water, sol conc HClAq

Reactions -1 PCl, forms the compound CH, NCCO CCl -> Y C,H, crystallising from alcohol in white needles [201°] -2 Alcoholic potash forms C,H,N(CH.,CO,H) CO CH, NHC,H, a white crystalline solid [129°] decomposed by conc HClAq at 160° into MeCl, o toluidine, and

C H NH CH, CO₂H Salt — (C₁₈H₁₈N₂O₂),H₂PtCl₂4aq [176°] Dı oxy di p tolyl-pyrazıne Dihydride Formed from oxalic acid and p tolyl amido-acetic p toluide (B a N) Made also by boiling the bromo acetyl derivative of p toluidine with alcoholic potash, or by heating p tolyl amido acetic acid at 200° (Abenius, J pr [2] 40, 433) Long white needles, insol water, m sol alcohol
Di oxy op di-tolyl pyrazine Dihydrid

Dihydride [1 2] $C_{\bullet}H_{\bullet}Me.N < C(OH)COH)NC_{\bullet}H_{\bullet}Me[1 4]$

[180°] Made by heating p-toluidine with the chloro acetyl derivative of o tolyl amido acetic acid at 140° (Abenius, J pr [2] 40, 448) White matted needles, v sol hot alcohol, insol ether

Tetra-oxy di phenyl-pyrazine. Dihydride of the di-sthyl derivative

 $[1\ 4]C_0H_4(OEt).N < \stackrel{OH_2CO}{CO} > N\ C_0H_4(OEt)[4\ 1]$

Stender needles

OXY p TOLYL QUINAZOLINE C₁₅H₁₂N₂O *. s

C₂H₄ CO N C₃H₄Me [146°] Made by oxidis-[146°] Made by oxidising p-tolyl quinazoline dihydride with KMnO4 (l'aal a Busch, B 22, 2698) Plates (from dilute alcohol) or needles (from ether), al sol. hot water Does not react with hydroxylamine or phenyl-hydrazine —B'HCl [214] Needles — B',H,PtCl, [abève 800°] Golden plates, sol alcoholic HO

OXY₅(Py 8) TOLYL-QUINOLINE C₁,H₁,NO i.e C₁H₂,NO CH COH). \$\psi\$ Flavenol.

Vol. III.

[196°] Got by the diazo reaction from (4,3,1)amido tolyl-quinoline (Weidel a Bamberger, M 9, 104) Small plates (from alcohol) Yields (Py 3) tolyl-quinoline on distillation with zinc-dust, Reduction followed by potash-fusion yields oxy-isophthalic acid —B'HCl 2aq —B'₂H₂PtCl₄ (dried at 105°) Yellow needles

Acetyl derivative C₁₆H₁₅NO₂ [106° Di-oxy-tolyl-quinoline C₁₆H₁₃NO₂ [80 [89°] Formed, as well as oxy-tolyl quinoline, by the above method of preparation Plates (from

alcohol), sol. benzene
DI-0XY-DI-0 TOLYL SULPHIDE C14H14SO2 S(C.H.Me(OH)[2 1 4]). Droxythrotoluene [135°] Formed from di-amido di-tolyl sulphide by the diazo-reaction (Truhlar, B 20, 676) Amorphous, sl sol water, alcohol, and ether

Di oxy - di - tolyl sulphide [210°-215° Formed from m cresol by treatment with SCl. in CS₂ (Tassinari, G 17, 92, C C 1888, 1354) Yields an acetyl derivative [44°], which forms, on oxidation, the corresponding sulphone [263°], which on saponification gives SO₂(C₇H₄OH),

Di oxy-di-tolyl sulphide [118°] from p cresol and SCl. Yields an acetyl derivative [84°] which is oxidised by KMnO, to a sulphone [209°], which on saponification gives SO₂(C,H_eOH)₂ [209°] (Tassinari, Rend Accad Linc [4] 4, 47)

ν OXY-0 TOLYL-THIO-UREA C₂H₁₀N₂SO ιε C₂H₄Me NH CS NH OH [92°] Formed from o tolyl thiocarbimide and hydroxylamine in chloroform solution (Tiemann, B 22, 1939, Voltmer, B 24, 381) Slender needles, almost insol chloroform and water, sol alcohol, ether, and KOHAq FeCl. colours its alcoholic solu-tion violet Yields o tolyl-cyanamide on long standing

Bensylether C.H. Me NH CS NH OCH, Ph [125°] Made from benzyl hydroxylamine and

o tolyl-thiocarbimide

 ${
m C_8H_{10}N_2O_2}$ te [c 180°] Formed ∞-OXY-0-TOLYL-UREA CH₂(OH) C₅H₄ NH CO NH₂ from amido benzyl alcohol, potassium cyanate, and HCl (Söderbaum a Widman, B 22, 1668) Tables or prisms, m sol boiling water, v sl sol alcohol Decomposes on fusion, yielding dioxy-di-tolyl-urea CO(NH C,H, CH,OH), [108°], which crystallises in needles

OXYTROPINE C,H,,NO $[242^{\circ}]$ occurring in crude belladonnine (Merling, B 17, 384, Ladenburg, B 17, 153) Crystalline —

B',H,PtCl, xaq red prisms
OXY TRUXILLIC ACID

(O₆H₄(OH) CH CH CO₂H)_x [273°]. Formed by potash fusion from (a)-sulpho truxillic acid (Lie bermann a Bergami, B 22, 783) Prisms, m Probably a polymeride of psol cold water An isomeric acid, formed from coumaric acid the amido- acid by the diazo- reaction, does not melt at 360° It yields an acetyl derivative [244°] (Homans, B. 24, 2591

OXY-URAMIDO-BENZOIC ACID derivative NH, CO NH C_eH_e(OMe) CO_eH Anisuramic acid S 05 at 100° Formed from potassium cyanate and a solution of the hydrochloride of amido-anisic acid (Menschutkin, A

3, 99) Needles (from water) — CaA', 7aq
OXY-UREA NH, CO NH OH [180°] Formed from aqueous hydroxylamine nitrate and potas786 OXY-UREA

sium cyanate in the cold (Dressler & Stein, Z. [2] 5, 202) Needles (from alcohol) v. e sol Aq. Decomposed by heating, yielding urea Reduces AgNO, FeCl, gives a blue-violet colour — KH(CH₄N₂O₂)₂ crystalline pp, got by adding alcoholic potash to the alcoholic solution (Hodges, A 182, 214) — (Pb,H(OAc),(CH,N,O₂), crystals — (CuCH,N,O₂), HOAc green mass Bensyl ether NH, CO NH OCH,Ph [188°]

Formed from (a) benzyl hydroxylamine hydrochloride and potassium cyanate (Behrend a.

Leuchs, A 257, 203) Needles

Oxy-biuret C2H5N2O3 [134°] Formed from cone hydroxylamine sulphate and potassium cyanate, the mixture being evaporated with Minute four sided prisms, sol water and alcohol Gives a white pp with AgNO, Reduces warm ammoniacal AgNO, FeCl, gives no colour — KC, H, N, O, minute needles

(a) - OXY - UVITIC Cresol dicarb-ACID C.H.Me(OH)(CO.H), [1 2 3 5] Cresol dicarboxylic acid [285°] (B), [295°] (H a R), [278°] (J) Formed from (a)-amido-uvitic acid by the diazo reaction (Böttinger, B 9, 804, 13, 1934, A 189, 177) and by potash-fusion from sulphouvitic acid (Jacobsen, A 206, 187, Hall a Remsen, Am 2, 137) Needles (from alcohol), v sol alcohol, insol chloroform Decomposes on sell, 4m 2, 157) Results (time stoom), v son datoohol, i nsol chloroform Decomposes on fusion Conc HClAq at 200° yields o cresol FeCl₂ gives a purple colour—Ca(HA''), 2aq—CaA'' 2aq—CaA'' 4aq—Ca₂(c₂H₁O₃),—Ag₂A''.

Methyl ether Me₂A'' [128°] Needles

Mono-ethyl ether EtHA''aq Needles

(8)-Oxy-uvitic acid

C₀H₂Me(OH)(CO₂H),[1 4 3 5] [225°-235°] (J), [220°] (B) S 13 at 12°, 5 2 at 100° (J) Formed by the action of nitrous acid on (β) . amido uvitic acid (Bottinger) Formed also by potash-fusion from s mesitol C₆H₂Me₂ OH and from oxy mesitylenic acid (Jacobsen, A 195, 285) Needles (from water), v sol alcohol and ether FeCl, gives a red colour HClAq at

200° forms p cresol (J) —Ag₂A" prisms

Methyl ether Me₂A". [79°] Needles

acid Oxy-1 uvitio $C_eH_2Me(OH)(CO_2H)_2$ [1346] Got by saponification of its ether which is formed from sodium acetoacetic ether by the action, in presence of NaOEt, of chloroform, chloral, trichloro acetic ether, or CCl, (Oppenheum a Pfaff, B 7, 929, 8, 884, 9, 821, Conrad a Guthzeit, A 222, 249) Needles, sl sol cold water, v sol alcohol and ether FeCl. gives a reddish violet colour. Softens at 290° decomposing at the same time Yields m cresol on distillation with lime PCl, forms a mixture of chlorides, whence water forms oxyuvitic acid and Cl. H., O. crystallising in needles —K.A" aq —BaA" 1½ aq —CaA" 1½ aq —CuA" —Ag.A" Methyl ether Me.A" [108°] Plates

a OXY.VALERIC ACID C.H.,O. 16 L. OH. CH. CH(OH) CO2H [81°] CH, CH, CH, CH(OH) CO,H by the action of HClAq on its nitrile, which is the cyanhydrin of n-butyric aldehyde (Menozzi, G. 14, 46) Got also by boiling a-bromo-butyric ether with aqueous Na, CO, (Juslin, B 17, 2504) Silky hygroscopis lamins, v sol water, alcohol and ether —BaA'; \$aq plates —CaA', S 86 at 100° —ZnA'; 2aq S 101 at 100° —CdA', .-CuA', —AgA'. small scales, sl sol cold water.

Ethyl ether Eth'. (190°). Oil.

a-Oxy-isovaleric acid (CH₂)₂CH CH(OH) CO₂H. [88°].

Formation —1. By heating bromo isovaleric acid with Ag₂O and water (Clark a Fittig, 4 139, 199) or with KOHAq (Ley a Popoff, A 61, Schmidt a Sachtleben, A 198, 87) —2' By digesting chloro-isovaleric acit with baryta. water (Schlebusch, 4 141, 822) -8 From its ether, which is a product of the action of zinc and isopropyl iodide on oxalic ether (Markownikoff, Z 1870, 517) -4 From its nitrile, which is made by combination of HCy with isobutyric aldehyde (Lipp, A 205, 24)

Properties —Rectangular tables, v sol water, alcohol, and ether Not deliquescent Volatile with steam Dilute H.SO, at 140° splits it up

Into isobutyric aldehyde and formic acid

Salts—NaA'—BaA',—ZnA', —CaA', aq—
CaA', 1; aq—CaA', 4aq—MgA', 2aq—CuA', aq

—AgA' feathery crystals (from hot water)

Ethyl ether EtA' (175°) Oil
Anhydride C.H.O. Valerolactide [126°] (220°-240°) Made by heating the acid in sealed tubes at 200° Needles, v sol alcohol and ether

Not attacked by dilute analysis Amide Pr CH(OH) CONH, [104°] from the nitrile and HClAq Crystals Pr CH(OH) CN 8 G \$ 96 Oil. decomposed at 136° into isobutyric aldehyde and HCy

a-Oxy-valeric acid CMeEt(OH) CO.H [68°]

(M), [66°] (B)

Formation -1 By saponification of its ether, which is made by the action of zinc on a mixture of MeI, EtI and oxalic ether (Frankland a Duppa, A 135,87) —2 By boiling OEtMeBr CO, H with baryta water (Böcking, A 204, 14) -8 From methyl ethyl ketone by combination with HCy and saponification of the resulting nitrile (B) 4 By oxidation of CMeEtH CO.H with dilute KMnO. (Miller, A 200, 282)

Properties - Needles (by sublimation), v e sol water, alcohol, and ether Oxidised to methyl ethyl ketone by chromic acid mixture Reduced

by HI to CMeEtH CO.H Rotates on water Salts —ZnA', —AgA' Nodules Ethyl ether EtA' (165 5°) SG 12 ((165 5°) S G 12 977 VD 498 (calc 504) Liquid, sol water

B-Oxy-isovaleric acid (OH₂)₂C(OH) CH₂ CO₂H

Formation -1 By oxidation of the alcohol OMe₂(C₃H₅) OH with cold chromic acid mixture (Saytzeff, A 185, 163, 197, 78), or with KMnO, at 0° (Schirokoff, J pr [2] 23, 206) —2 By the action of zinc on a mixture of acetone and chloro acetic ether (Reformatsky, B 20, 1210) -8 By exidation of tri exy hexane by KMnO.

(Reformatsky, J pr [2] 40, 404)
Properties — Syrup, v sol water, alcohol, and ether Not volatile with steam Reduced by

HI to isovaleric acid

Salts - CaA', 12aq - CuA', - CuA', 2aq. -AgA' monoclinic crystals, sl sol water. Ethyl ether EtA' (180°)

β-0xy-valeric acid CH, CH(OH) CHMe CO,H Formed by reduction of methyl-acetoacetic ether with sodium amalgam (Rohrbeck, 4 188, 229) Syrup, resolve 1 by distillation into water and methyl-crotonic acid [62°]—NaA' (dried at 100°). [210°] (Miller, 4

200, 269) Orystalline powder —BaA', aq — AgA laminæ, si sol hot water

 (γ) -Oxy-valeric acid

CH, CH(OH) CH2-CH2-CO2H The salts of this acid are made by dissolving the lactone in bases The free soid quickly changes back to the lactone

Salts — The Ba and Ca salts are deliquescent amorphous masses -AgA' triclinic needles

Ethyl ether EtA' Oil.

Lactone CH, CH CH, CH, CH, (208° 1 V) SG 2 1072 Occurs in crude wood vinegar (Grodski, E 17, 1369) Prepared by boiling y bromo valeric acid with water (Messerschmidt, A 208, 96), and by reduction of acetyl propionic (levulic) acid with sodium amalgam (Wolff, A 208, 104) Formed also by heating γ-oxy propylmalonic acid (Hjelt, A 216, 56), and by the action of NaOHAq on nitroso oxy methyl pyrrole dihydride (Tafel, B 22, 1864) Liquid, miscible with water Neutral to litmus Separated from solution by K.CO. Reduced by HI and P at 250° to n-valeric acid Oxidised by HNO, to succinic acid Boiling alcoholic NaOEt forms C₁₆H₁₄O₂ [c 82°] (Fittig, A 256, 126) Phenyl hydrazine forms C₁₁H₁₆N₂O₂ [76°-79°], orystallising in needles, v sol water (W Wishcenus, B. 20, 402)

Amide CH, CH(OH) CH, CH, CONH, [56°] Formed by heating the lactone or the ether with NH, Aq Thin plates, v e sol water and alcohol, sl sol ether At 170 it is split up into NH, and the lactone (Neugebauer, A 227, 97)

Di-oxy-valeric acid

CH, CH(OH) CMe(OH) CO.H Di-methyl gly ceric acid [107°] Formed by the action of water at 99° on di methyl glycidic acid

O CMe CO.H [62°], which is formed from tiglic acid OH, CH CMe CO2H by successive treatment with HOCl and boiling KOHAq (Meli koff, A 234, 228, Bl [2] 47, 166) —KA' —AgA'
Tetra-oxy-valeric soid C,H₁₀O₆ t c

CH₂(OH) CH(OH) CH(OH) CH(OH) CO₂H Arabonic acid [a]₀ = -67° Formed by allowing arabinose (10 g), water (75 g), and Br (20 g) to stand for 36 hours (Bauer, J pr [2] 30, 379, 34, 46, Kiliani, B 19, 3081, 20, 344) Hygroscopic crystalline mass —CaA',5aq —SrA',5aq prisms

References -BROMO and CHLORO- OXY-VALE-

RIC ACID

TETRA-OXY-VALERIC ALDEHYDE

CH,(OH) CH(OH) CH(OH) CH(OH) CHO Arabenose [160°] Mol w 150, by Raoult's method (Brown a Morris, C J 53, 619) H C p 557,100 (Brown a Morris, C J 53, 619) H Cp 557,100
H.F 259,400 (Berthelot, C R 111, 12) A product of the hydrolysis of Arabic Acid (g v)
(Scheibler, B 1, 58, 108, 6, 612, 17, 1731, Kiliani, B 13, 2804, 15, 87, 19, 8081, 20, 344, Claesson, B 14, 1271, O'Sullivan, C J 45, 41) Trimetric prisms, v sol hot water, nearly insol alcohol and ether Dextrorota tory (v vol 1 p 297) Tastes sweet Does not undergo alcoholic fermentation Yields a phenyl-bydraude [1582] Arabium C. H. O. 18 an an hydrazide [158°] Arabinin C₁₆H₁₆O, is an an hydride of this aldehyde (O'Sullivan, C J 57, 59).

OXY-VALERO-CYAMINE v a-GUANIDO-VA-

LERIC ACTO

OXY-VINYL-BENZOIC ACID Anhydride e. Methylene-pathalide

OXY-XANTHOME o OXY-DEPHENYLENE ES-TONE OXIDE

OXY-XYLENE v. XYLENOL and TOLYL-CARB-

Di-oxy-xylene The (6,3,2,1)-, (5,2,3,1)-, and (5,2,4,1) di oxy-xylenes are described as Hydro-XYLOQUINONES OXY-TOLYL-CARBINOL is an w-680di-oxy xylene (5,8,4,1)-D1-oxy-xylene is described as BETOROW

Di-oxy-m-xylene C.H.Me.(OH), [1 8 4-6].

Xylorcin Mol w 188 [125°] (278°) Formed from amido m xylenol [161°] by the diazo- reaction (Kostanecki, B 19, 2324) White mono-clinic plates (from chloroform), v sol water, alcohol, and ether Not affected by air containing NH,

Di-acetyl derivative C.H. (OAc). [45°]. (286°) Prisms, insol cold water

Di oxy xylene C.H.Me.(OH). [1200] by potash fusion from chloro m xylene sulphonic acid (Gundelach, Bl [2] 28, 345) Gives a red colour with bleaching powder solution

D1-0xy-m-xylene C₆H₂Me₂(OH)₂[1 8 2 4] [146°] Formed from m-xylene by heating with H₂SO, at 150°, converting the resulting disulphonic acid into chloride and fusing the C.H.Me. (SO. Cl.), with potash (Wischin, B 23, 3113) White needles (by sublimation), v sol. water, alcohol, and ether FeCl, colours its solution deep violet Fusion with phthalie

anhydride forms a fluorescein

Di-w-oxy-o-xylene O.H. (CH, OH), Phthal-alcohol o Tolylene alcohol Xylylene alcohol. Di methyl benzene glycol [64°] 8 (ether) 25 at 18° Formed by the action of sodium amalgam upon a boiling solution of phthalyl chloride in HOAc (Hessert, B 12, 646) Formed also by boiling di & bromo-o-xylene with Na,CO,Aq (Baeyer a Perkin, jun, B 17, 124, C J 58, 6; Colson, C R 98, 1643, Bl [2] 48, 6, 45, 6; A Ch [6] 6, 106) Tables (from ether), v e sol. water and alcohol HBr forms C₂H₄(CH₂Br), and HCl acts in like manner KMnO, oxidises it to phthalic acid Resinified by cold H₂SO, Hot H.SO, forms amorphous insoluble (C.H.O), and syrupy C₁₆H₁₈O₅ (Hjelt, B 19, 1588) HNO₅ forms phthalide

halide
De acetyl derevative C₁₂H₁₄O₄ [87°]
C.H.(OEt)₂. (248°) at

Dt ethyl ether C_tH₅(OEt). (248°) at 720 mm Lquid (Leser, B 17, 1825)

D1-\(\omega\) coxy m-xylene C₅H₄(CH₂OH). [47°].

SG (lquid) \(\frac{12}{2}\) 1 161, \(\frac{82}{2}\) 1 135 Formed by boiling O.H. (CH.Dr.), [77°] (1 mol) with water containing K.CO. (1 mol) (Colson, A Ch [6] 6, 112, O.R. 99, 40) Got in like manner from C_eH₄(CH₂Cl)₂ (Colson a Gautier, Bl [2] 45, 6) Crystalline solid, with bitter taste, v e sol water and alcohol, m sol ether HBr regenerates diw-bromo-m xylene Gives isophthalic acid on oxidation

Ethyl ether C.H.(CH.OEt)_r (248°) at 712 mm Got by boiling C.H.(CH.Br)₂ with alcoholic potash (Kipping, B 21, 46, C J 53, 46) Oil Yields isophthalic acid on existing.

Di-s-oxy-p-xylene C.H. (OH. OH). p-Xylenyd alcohol. [113°] Formed from C.H. (OH. Ol. of boiling NaOHAq upon terephthalic aldehyde (Löw, A 281, 874) Needles, v. sol. water, alcohol, and ether. Yields terephthalic acid on oxidation.

Acetyl derivative C.H. (CH. OAc), [47°] Made from C.H. (CH. Cl.), and KOAc in alcohol. Bensoyl derivative C.H.(OH2OBE)2.

Needles, v sol alcohol and ether (Grimaux)

Mono-ethyl ether C.H. (CH2OH) (CH2OEt) (251°). Oil. Formed from di a-chloro-p-xylene and cone alcoholic potash at 100° (G) Successive treatment with PCl, and water converts it into terephthalic aldehyde (Colson, C R 99,

975) Tri-oxy-xylene C.HMe2(OH), Formed by reducing oxy-isoxyloquinone with aqueous SO₂ (Fittig a Siepermann, A 180, 37) Crystallises from water in tables (containing aq). Melts at 90° when hydrated Colours the skin brown On spontaneous evaporation of the aqueous solution in air it forms a quinhydrone as dark lustrous needles [143°] Yields m xylene on distillation with zine dust

Tri-acetyl derivative [99°] Prii Reference — Tetra chloro di oxx-xxlene [99°] Prisms DI-OXY-XYLENE CARBOXYLIC ACID CeHMe2(OH)2CO2H[13465] Xylorcin carb oxylic acid [196°]. Got by heating m-xylorein with NaHCO, and some water at 130° (Kostanecki, B 19, 2323) Prisms from dilute alcohol), al sol water Gives off CO, on fusion

FeCl, gives a deep blue colour

Oxy-m-xyloquinone C,HMe2(OH)O Formed by distilling di amido mesitylene with chromic acid mixture and water, Me being displaced by OH (Fittig, B 8, 16, A 180, 27) Orange needles, smelling like quinone, m sol hot water, v e sol alcohol and ether Volatile with steam. Its alkaline solution is reddish violet Reduced by SO, to tri-oxy-xylene Acetyl chloride at 100° forms a crystalline body [124°], insol water CsH,Os(OK) Small black needles, v Aq, m sol alcohol, insol ether -(C,H,O,),Ba

Brownish-red pp a-OXY-XYLYL-ACETIC ACID

[1 8.4] C,H,Me,CH(OH) CO,H [119°] reducing (1,3,4)-xylyl glyoxylic acid (Claus, J pr [2] 48, 148) Rhombohedra (by sublimation), v. sl. sol. cold water, v sol alcohol and ether

a-Oxy-xylyl-acetic acid 1 4 2 C.H.Me. CH(OH) CO.H [114°] Got in from [1 4 2] C.H.Me. CO CO.H like manner aus) Needles or prisms, v sol hot water DI-OXY-XYLYLENE DI-METHYL-DI-

 $C_{H_*}(CH_*C \leqslant_N^N C(OH) > CH)_*$ PYRIMIDINE Made from acetoacetic ether and Tabove 250°1 p-phenylene-diacet imido- ether (Glock, B 21, 2661) Crystalline mass, insol ordinary solvents OXY-XYLYL-METHYL-PYRAZOLE

 $C_eH_eMe_s.N < N = CMe$ [159°] Got from the product C₂₂H₂₄N₄O₄ of the action of (1,8,4). xylyl-hydrazine on acetoacetic ether by heating with cone HClAq at 150° (Klauber, M 12, Small white needles —B'HOl [185°] — B',H,FeOy, , white crystals Oxy-xylyl-di-methyl-pyrazole

 $C_{\bullet}H_{\bullet}Me_{\bullet}N < CO - CH \\ NMe CMe$ [118°] Made by heating the compound C.H., N.O. (v supra) with MeI and MeOH at 180° (K) Small white needles, v sol alcohol and ether, sol cold water Reduces Fehling's solution FeCl, gives a violet red colour —B'HCl [95°]. Small crystals

DI-OXY-DI-XYLYL-PYRAZINE DIHY

 $C_0H_2Me_2N<_{OH_2}^{OO}CH_2>N C_0H_2Me_2$ DRIDE [203°] Formed by boiling brome acetyl (1,',2) xylidine with alcoholic potash (Abenius, J pr

[2] 40, 436) Flat needles, insol water and ether OZOKERIT A fossil resin, consisting chiefly of a hydrocarbon called lekene $(q \ v)$ On chlorination in presence of SbCl_s at 360° it yields CCl₄, C₂Cl₆, C₄Cl₆, and C₆Cl₆ (Hartmann, B 24, 1019) (V also Parappin)

OZONE O, Mol w 47 91 A blue gas (Hautefeuille a Chappuis, O R 91, 522), it usually occurs mixed with oxygen, and possesses a characteristic odour (-106°) (Olszewski, M 8, 69, W 37, 337) VD 24 S at 760 mm. 366 at 18° (Schöne, B 6, 1224), 834 at 1° (Carius, A 174, 80), and 2745 at 14° (McLeod, C J 49, 607) Andrews states that it is insoluble in water

Occurrence.—Ozone is believed to be a normal constituent of pure air Hartley ($C\ J\ 39, 111$), Chappuis ($C\ R\ 91, 985, 94, 858$), and E Schöne ($J\ R\ 1884\ 2, 250$), who have examined the absorption spectrum of ozone, have attributed the blueness of the sky to its presence But the recent observations of Liveing a Dewar $(P\ M'[5]\ 26,286)$ show that the absorption spectrum of compressed oxygen exhibits certain bands identical with those of the solar spectrum, which Angstrom found to be equally strong whether the atmosphere was wet or dry, and that daylight when observed through a column of oxygen 18 m in length and at 90 atmos possesses a blue tint (v also Olszewski, W 42, 663) The proportion of ozone in the air varies very considerably, and is supposed by many observers to be greater at high than at low altitudes (v also Thorpe, C J Proc 72) Houzeau judges the maximum pro portion at ordinary levels to be $\frac{1}{700000}$ by volume (C R 74, 712) Andrews found that a tempera ture of 250° destroys the constituent of the air which exhibits the reactions of ozone, whereas air containing traces of chlorine, or of the higher oxides of nitrogen, is not so affected by heat (Pr On the other hand, Ilosvay (Bl [3] 2, 16, 68) 877) and Schöne (B 13, 1503) conclude that the presence of ozone in the air is still unproved

Formation - 1 Ozone is formed in the electrolysis of dilute sulphuric acid (Schönbein, P 50, 616, Marignac, C R 20, 808, Meidinger, A 88, 57, C J 7, 251, Baumert, P 89, 38, Andrews, T 146, 1, Soret, Arch des Sciences, 16, 218, O R 56 390, Berthelot, O R 86, 71, A Ch [5] 14, 345, Schöne, B 6, 1224, Carus, A 174, 1, Brodie, C J 17, 293, McLeod, C J 49, 591) Berthelot and Schönbein also obtained ozone by the electrolysis of other acid solutions It has been supposed that the ozone formed in electrolysis is accompanied by $H_{*}O_{*}$, but Brodie (C J 17, 281), and, more recently, McLeod (loc cit), have shown that the oxidising body which remains in solution is probably S.O. The proportion of ozone present in electrolytic oxygen appears to depend to a great extent on current-density By using a positive electrode of very small area McLeod obtained O containing 17 4 per cent of ozone, when electrodes of large

OZONE 780

area are used the yield of ozone is sometimes very small.—2 When are or oxygen is exposed to the electric discharge, especially if it be the silent discharge, the O is partly converted into osone If air be used, oxides of N may be formed and mistaken for ozone According to Berthelot $(O\ R\ 92,82)$ and Hautefeuille a Chappuis $(O\ R\ 92,80)$, and 134), oxides of N may be formed to a slight extent even by the silent discharge, and H and C have obtained a new and unstable oxide Giannetti a Volta (G of nitrogen in this way 5, 439) found that with the discharge from a Holtz machine the yield of ozone is increased by using a wire brush as negative electrode Bichat a Guntz (C R 107, 834, A Ch. [6] 19, 131), who used an ozone generator consisting of a wire stretched along the axis of a metallic tube, found that the negative effluve produced by far the greatest yield of ozone. This they attribute to its higher temperature. It has been suggested that the production of ozone by the electric discharge is an effect of a condition of electro static stress But Thomson a Threlfall (Pr 40, 329) find that oxygen is only converted into ozone when there is an actual luminous discharge This has been confirmed by Bichat a Guntz, and some experiments by the writer seem to show that even when oxygen is illuminated by the ultra violet rays ozone is only formed by actual luminous discharge Dewar has obtained a body giving the reactions of ozone from air by pressing a current of water through a glass tube, surrounded by a larger tube of platinum which was heated by the oxyhydrogen flame, the air from the annular space between the hot and cold tubes being sucked into the inner tube by the stream of water through a minute hole in the glass tube, and collected and examined If the substance thus obtained was really ozone, this result seems to confirm the idea that the action of the electric discharge on oxygen is due to temperature (v. also Elster a Gentel, W 39, 321, and Ilosvay, Bl [8] 2, 784)

The formation of ozone from O by electric

discharge is greatest at low temperatures and under high pressure (von Babo, A 1863 Suppl. 11, Hautefeuille a Chappuis, C R 91, 228) But the exact influence of temperature and pressure have probably not yet been made out. Hautefeuille a Chappuis have noticed that at a pressure of about 50 mm ozone is alternately produced and destroyed by the silent discharge Von Babo a Claus, and Haute (C R 94, 646) feuille a. Chappuis, consider that prolonged ac tion of the discharge is favourable to ozonifica tion But Brodie, with the apparatus described below, found that the maximum effect was quickly reached. The writer's experience agrees with that of Brodie, and tends to show that observations to the contrary effect have been due to the irregular working of the machine employed

Bichat a. Guntz, using the apparatus described above, have failed to find any simple quantitative relation between the potential difference of the discharging surfaces and the yield of ozone, though they, and also Giannetti a. Volta (G. 5, 489) and Berthelot, find that an increase of potential produces an increased yield of osone. (For details on various points v. Marignae a. De la Rive, Arch of Elect. 5, 5; Fremy a Bec-

querel, A Ch [8] 85, 62, Andrews, T. 146, 1; 150, 118, Brodie, T 162, 435, Berthelot, C R. 88, 50, A Ch [5] 12, 448, Hautefeuille a. Chappuis, C R 92, 80, 134, 94, 646, Shenstone a Cundall, C J 51, 610) Hautefeuille a. Chappuis (C R 91, 762) find that the production of ozone by the action of the electric effluve on oxygen is prevented by the presence of Cl, but that N, H,

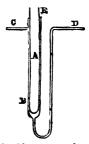
and SiF, are favourable to its production 8 Brodie (T 164, 83), by the action of the silent discharge on carbon dioxide, under the most favourable conditions, obtained as much as 85 p c of the liberated oxygen in the form of ozone

Ozone has long been regarded as one of the products of various cases of oxidation such as the slow oxidation of P, Et,O, and turpentine, the decay of organic matter, and the combustion of compounds containing H in the air, Thorpe a Tutton observe that it is not formed in the oxidation of P_4O_6 (C J 57, 569) It is possible, however, that ozone is less frequently formed in such changes than has been supposed, and that the reactions attributed to ozone may often have been due to H_2O_2 . The experiments of Kingzett (C J 37, 792) and McLeod (C J 37, 118), how ever, seem to make it certain that ozone is produced in the slow oxidation of P (v also llosvay, Bl [3] 2, 360, 4, 707, Leeds, C. N 39, 157, 40, 70, 41, 164, 42, 17, Cundall, C J Proc 78, 26, Loew, B 22, 3325)

Heat of formation —30₂ = 20₃ = -59,200 (Berthelot, C R 82, 1281), —66,720 (Mulder a van der Meulen, B 15, 511)

Preparation —1 From oxygen The fol

lowing method, which was introduced by Siemens and Brodie, is perhaps the most convenient A tube, A, is sealed into a slightly larger tube B,



at E, before the blowpipe, or by means of solid paraffin A and B should be of thin glass, and paraffin two narrow tubes, C and D, should be attached to B A is filled with dilute H.SO, and the apparatus is then immersed in dilute acid to the level CD, the electrodes of a Ruhmkorff coil, or of an electric machine, are respectively connected with the acid in A, and the contents of the cylinder, and a slow current of O is led through the apparatus from D to C while the discharge passes. The liquid in the cylinder should be cooled by ice, or it may be replaced by a freezing mixture, in which case a platinum wire should be wrapped round the outside of B The gas which escapes at C is well charged with ozone The ozonised oxygen may be collected over oil of vitriol. It must not be brought into contact with indiarubber; joints that will bear contact with oxone may be made by slipping a wider tube over the

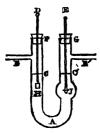
OZONE 790

ends of those that are to be connected, warming them, and running a little melted paraffin be-tween the inner and outer tubes

The character of the discharge in the ozone generator has been studied by Hautefeuille Chappuis (C. R. 91, 281), Thomson a Threifall (Pr 40, 329), Shenstone a Cundall (C. J. 51, 622), and by Biohât a Guntz (A. Ch. [6] 19, 181)

2. By electrolysis. When dilute H₂SQ, is

electrolysed with electrodes of considerable area the proportion of ozone in the O is usually small McLeod (C J 49, 591) recommends the following method Place dilute H₂SO₄ (S G. 11) in a U tube, A, attach delivery tubes to the



arms BB' Let the negative electrode H be a sheet of Pt foil suspended by the glass D from a cork closing the mouth at F, and let the positive electrode J consist of two fine wires, sealed into a glass tube E, which is afterwards filled with mercury On connecting D and E with a galvanic battery, O highly charged with ozone will escape at B' It is best to immerse the U tube in ice cold water McLeod has obtained O containing as much as 173 pc of ozone by means of this apparatus

3 To prepare ozone by the oxidation of phosphorus Place clean sticks of P half submerged in water in a series of flasks, and conduct a rather slow stream of air through the flasks, and then through a little water A temperature of 24°-25° gives the best results H₂O₂ is also formed, but it remains dissolved in the water

(Kingzett, C J 37, 792)

Properties and Reactions — Ozone is more strongly magnetic than common oxygen (Becquerel, C R 92, 348) Its rate of diffusion is near to that required for the density 24 (Soret, A Ch [4] 13, 257) It is entirely destroyed at 270° (Andrews, T 150, 113) by contact with platinum black at ordinary temperatures (Mulder a van der Meulen, B 1, 167), and on contact with pure Hg (Hg is not visibly oxidised it both be perfectly dry, Shenstone a Cundall, O. J 51, 619) Ozone is also decomposed by dry Ag, the silver being but slightly oxidised, and by contact with MnO₂ (Andrews) Volta (G 9, 521) states that Au, Pt, Pd, and dry Ag are without action on ozone Brodie came to a similar conclusion in regard to Au, Al, and Berthelot (C R 86, 76) and others have Cu considered that dry ozone has no fixed pressure of dissociation If suddenly compressed, or compressed without cooling, it explodes with yellowish fiame (Hautefeuille a Chappuis, C. R. 91, 522). The action of ozone on salts has been studied by Maquenne (C. R 94, 795), and by Mailfert (C. R. 94, 860). The latter has also

studied its action on S, Se, Te, and several sulphides, and on CH₄, C₂H₄, C₂H₅, C₅H₁₀, C₄H₆, and C₂H₆ (C, R, 94, 1186) Ozone oxidises alcohols of small molecular weight more readily than the polyhydric alcohols (A Renard, A Ch [5] 16, 289) Liquid ozone explodes violently on corning into contact with C2H4 (Olsze iski, A Ch [2] 37, 837) It acts as a strong bleaching agent on vegetable colours, and quickly destroys india rubber, its action on cork is much less rapid It does not oxidise CO at 300° (Remsen, Am 4, 50) It oxidises NH, Aq, forming ammonium salts of nitrous and nitric acid (Carius, A 174, 31), unless the solution is dilute (Harriey, C.J 39, 123) It is believed to be completely absorbed by turpentine and oil of cinnamon (Soret, A Ch [4] 7, 113), peroxidised compounds being formed which react with water (Kingzett, C J 37, 800) When ozonised O acts on KIAq, I is set free and the ozone is destroyed, but the volume of the gas remains unaltered With neutral solutions the initial action may correspond to the equation $2KIAq + O_3 = K_2OAq + O_2 + I_2$, but usually KIO₃ is a final product of the change P glows freely in ozonised air (Thorpe a Tutton, C J 57, 571) Ozone oxidises TIOH and As2O2, the latter action has been used in determining its heat of forma tion It is destroyed by solutions of KHO, BaO, and CaO to a certain extent (Andrews) Hartley has observed the formation of peroxide of potas sium by its action on solid KOH (C J 39, 124) But it is unaffected by solution of Na₂CO₂ (Brodie) It readily attacks I, forming periodic acid and lower oxides of I (Ozier, C. R. 86, 722) It con verts ether into an ozonised substance which acts with water to form H₂O₂ (Kingzett, C N 34, 127, Berthelot, C R 86, 71, Dunstan a Dymond, C J 57,584) Several observers have concluded that it arrests putrefaction of animal matter, and have proposed its use as a preservative for meat When present in the air in large quantities it frequently produces irritation of the mucous membrane

Although its general action is that of a strong oxidiser, in certain cases ozone acts as a reducing agent Thus when ozone acts with Na₂O, an expansion occurs which is due to the simul taneous decomposition of the two bodies in equivalent proportions (Brodie, T 162, 454), probably according to the following equation $Na_2O_2 + O_3 = Na_2O + 2O_2$ Probably other unstable oxides, such as \dot{H}_2O_2 , react with it similarly under favourable conditions. Its action on blood has been said to resemble that of a reducing agent (Dogiel, C C 1875, Binz, C C 1882) It changes the red colour of the compound formed when sulphanilic acid is mixed with naphthyl amine to orange yellow (Ilosvay, Bl [ℓ] 2, 351)

Detection -Paper impregnated with TIOH is turned brown by ozone even when dry (Schöne, B 18, 1508) The similar change of colour pro duced by nitrous acid is destroyed by excess The colour is also permanent when ozone is mixed with a relatively small proportion of nitrous acid (Hosvay) The action of ozone on nitrous soid (Ilosvay) The sction of ozone on the red compound of naphthylamine and sul phanilic acid (v Properties) also affords a test for ozone, even in the presence of traces of nitrous acid (Ilosvay, Bl [3] 2, 860) Ozone may be distinguished from H_2O_2 by not yielding water when strongly heated, and by the absence

OZONE 791

of any action with titanic acid or chromic acid, also by resisting the action of Na,CO₂, which destroys H₂O₂ Papers saturated with solutions of KI and staroly are often used for the detection of ozone, but are only trustworthy when the absunce of Cl and of oxides of nitrogen can be assured Houzyau employed test papers steeped in faintly acid solution of litmus and then treated with KI These he found to be insensitive to O, to traces of oxides of nitrogen, and to H₂O₂ When exposed to ozone, however, they are turned blue by the alkali that is set free

are turned blue by the alkali that is set free

Estimation —1 Rough estimations of ozone are frequen ly made by comparing the tints produced by exposing some of the test papers men tioned above with a scale of tints Such methods are not very satisfactory -2 Thénard has estimated the proportion of ozone in the air volumetrically by means of a standard solution of As O in HClAq of such strength that 1 c c is equivalent to 1 mgrm of O 10 or 20 cc of the solution are thoroughly agitated with the sample of gas, 30 cc of a 1 pc solution of H2SO, are added, and it is then titrated in the usual manner with permanganate For 8 grms of O absorbed 24 grms of O, are destroyed (Berthelot, C R 82, As oxides of nitrogen and H₂O₂, if pre sent, tend to reduce the amount of ozone found, this method gives the minimum, and not the maximum, amount of ozone present -3 If a solution of potassium arsenite containing 73 grm per litre, with an excess of pure KI, be agitated with air containing of one, part of the arsenite is converted into arsenate by the ozone, and the amount of unaltered arsenite can be found by titrating with very dilute I solution after adding some ammonium carbonate and starch method is strongly recommended by Hartley (C J39, 120) The solution of the arsenite should be acidified for keeping, and neutralised before use with KHCO, -4 The action of ozone on KIAq may also be employed to estimate ozone iodide must be perfectly free from iodate, and must be thoroughly brought into contact with When the action is complete, and not the gas before, the product must be acidified with dilute HClAq or H₂SO₄Aq The liberated I may then be titrated in the usual manner The O equivalent to the I liberated, multiplied by three, gives the amount of ozone -5 The amount of ozone produced in the electrification of oxygen may also be calculated from the contraction that occurs under the influence of the discharge (v Babo, A Suppl 2, Andrews, T 150) Shenstone a Cundall (C J 51, 610) have devised an apparatus for this purpose S a C have shown that if the ozonised gas comes into contact with oil of vatriol in such a process, the acid should be previously thoroughly treated with ozone, otherwise the results are likely to be high

History —The earliest known record concerning ozone relates to an observation by van Marum, 1785, that air or O when submitted to the electric spark acquires a characteristic odour About fifty years later, 1840, Schombein, who published about sixty papers on this subject, published life first memoir on osone in Poggendorff's Annalen As the result of his numerous observations, Schönbein recognised ozone as a distinct form of matter, ascertained that it could be obtained by the electrolysis of dilute acid, by

means of the electric discharge on O, and in the slow oxidation of P And it is interesting to note that these still constitute the chief methods for the production of ozone He also observed many of its chief properties For several years after Schönbein's original discovery, comparatively little progress was made in ascertaining the nature of ozone till the experiments of Marignac and De la Rive, 1845 (Arch of Elect), and of Fremy and Becquerel, 1853 (A Ch [3] 35, 62), showed that the purest O then obtain able could be entirely converted into ozone, pro vided that the action of the spark took place in the presence of excess of KI, or of moist silver, which appeared to be capable of completely ab sorbing ozone But it was not till a much later period that the researches of Andrews (T 146, 1)and Soret (C R 56, 390) finally showed that ozone from all sources is identical Although the researches of Marignac a De la Rive, and of Fremy a Becquerel, thus established the character of ozone and its production from oxygen, the exact relation of the two bodies was still imperfectly understood, and ozone seems to have been regarded as differing from oxygen either in regard to its electrification, or, by some, in being a compound of oxygen and water, until in 1860 Andrews and Tait (loc cit) examined the volumetric relations of ozone and oxygen. and by a masterly research showed that the ozonising of oxygen is accompanied by a con traction in the volume of the gas, and that, on the other hand, the reproduction of O from the ozone by heat causes the gas to recover its ori ginal volume In this research A and T also showed that the rodine titre of a sample of ozon used oxygen corresponds in every case to the contraction that has occurred on ozonising it, a fact which, in the hands of Soret and Brodie, materially contributed to the further elucidation of the subject Andrews and Tait also observed that when ozonised oxygen acts with KIAq, the gas remains unaltered in volume after the action is complete The true bearing of these facts was not, however, perceived till Odling (Manual of Chemistry) pointed out, in 1861, that they were consistent with the adoption of O, as the simplest formula for ozone This interpretation was afterwards supported by the experiments of Soret and Brodie The former showed that when ozonised oxygen is allowed to act on turpen tine, a contraction occurs that is equal to about twice the iodine titre of the gas, te is about twice as great as the contraction which accompanies its formation, from which, if it be assumed that the ozone formed is wholly absorbed by the turpentine, it follows that two volumes of gaseous ozone contain three volumes of gaseous oxygen Soret's experimental numbers did not agree very closely with this hypothesis But the hypothesis was confirmed by subsequent experiments, in which he compared the rates of diffusion of ozone, Ol, and CO,, and found that the rate of diffusion of ozone approximates to that of a gas having the S G 24 (A Ch [4] 18, 257) Finally, in 1872, Brodie (T 162, 485), as one of the results of a beautiful series of experiments, found that, while in some cases, as in that of neutral KIAq, the oxidation caused by ozone is unaccompanied by any contraction in the volume of the gas, in other cases various degrees of con792 OZONE.

traction occur Thus the oxidation of HIAq is attended by a diminution in the volume of the gas equal to half the volume that would be occupied by the weight of gas that is absorbed, and the action of the gas on turpentine and on Na S.O. Aq 18 accompanied by a diminution of volume equal to two-thirds of the volume that the O absorbed would occupy in the free state Intermediate contractions were observed, but in no case did the contraction seem to be greater than in the action of turpentine, a result which afforded strong confirmation of the views of

Soret and Odling An account of the early work on ozone exists in the Handwörterbuch der Chemse, 5, 835 (Braunschweig, 1853) (For later

work v Odling, R I 1872)

This name was formerly given Antosone to a substance whose action with ozone resulted in their mutual decomposition. Before the relations of ozone and oxygen were established, these bodies were by some supposed to consist of oxygen in opposite conditions of electrifica-Antosone was probably hydrogen per-W A S tion.

P

PACHYMOSE C₁₀H₂₄O₁₄ A substance, pro bably a glucoside, occurring in Pachyma pincto-rum, a Chinese fungus (Champion, J 1872, 789) Insol water, sol alkalıs, forming a solu

tion ppd by Ca and Pb salts

PACHYRHIZIDE A substance, not containing nitrogen, extracted from the seeds of Pachyrhizus angulatus (Greshoff, B 23, 3539) V sol alcohol, ether, and CHCl2, v sl. sol water and KOHAq Tastes bitter, and is extremely poisonous, especially to fishes. Begins to melt at 61°, and decomposes at 161° Yields salicylic and protocatechuse acids on fusion with potash The alcoholic solution is said in reaction Probably identical with a similar body in the rootbark of Derris (Pongamia elliptica)

PÆONOL C,H,O, t & CH, CO C,H,(OH)(OMe) [50°] Got from the bark of Pæoma montana of Japan (Nagai, B 24, 2847) White needles (from alcohol) Yields an acetyl derivative [46 5°], a phenyl hydrazide [107°], and a crystalline oxim (Tiemann, B 24, 2855) Potash forms resacctophenone CH, CO C,H, (OH),. HIAq

at 150° forms the same body

PALISANDER RESIN C21H22O.? [95°] SG 14 1 266 Extracted by alcohol from palisander wood, a red dye wood from Madagascar (Terreil a Wolff, Bl [2] 33, 435, of Arnaudon, Comento, 8, 278)

PÁLLADIUM Pd At w 1063 Mol w Melts between 1360° and 1380° Becquerel, C R 57, 855), at c 1500° (Violle, C R 87, 981) S G 11 4 at 22 5° (Deville a Debray, P M [4] 50, 651) For other numbers v Clarke's Table of Specific Gravities, 2nd edit, 15. S H = 0582 at 0°, = 0582 + 00002t at t° (Violle, l.c) Heat of fusion = 363 cals СE (linear) = 00001176 at 40° (Fizeau, C R 68, 1125) E C. 1264 at 172° (Ag at 0°=100) (Matthiessen, P 103, 428) Volatilises in green vapour at c. 2000° S V S c 9 3 For chief lines in emission-spectrum v B A 1884 434

Occurrence -In small quantities, about 2 p c., as metal alloyed with Pt, Ir, Os, Ru, and Rh. Certain kinds of South American gold contain from 5 to 10 pc Pd. Occurs also, with gold and lead selenide, in the Harz (Zinken, P 16, 491), and in small quantities in some specimens of silver (Rössler, A. 180, 240). In 1808 Wollaston (T. 1804, 428; 1805 816) separated two

new metals from Pt ore, to one of these metals he gave the name palladium, in allusion to the discovery, made about the same time, of the planet Pallas, and the other he called rhodium, because of the rose-coloured solutions of its salts (pobov = a rose)

Formation —1 By heating PdCy2-2 By heating PdCl, 2KCl and washing out the residual KCl —3 By ppn from solutions of its salts by means of Zn, Cu, or Fe - 4 By reducing

PdCl, 2KClAq by oxalic or formic acid

Preparation -- When P. ore is heated in aqua regia, the Pd goes into solution, along with most of the Pt, as PdCl2. From this solution Pd is obtained by various processes 1 The solution is made as nearly as possible exactly neutral by Na₂CO₂, and HgCy₂Aq is added, PdCy₂ is ppd, along with Cu₂Cy₂ if the ore contained Cu, the pp is washed, dried, and strongly heated, whereby Pd is obtained, mixed with Cu, the metallic residue is dissolved in HNO, Aq, the solution is neutralised by Na₂CO₃, and heated with HCO2KAq and H4C2OAq, whereby CO2 is evolved plentifully, and Pd is deposited in lus trous plates, while Cu remains in solution (Dobereiner), or the metallic residue obtained by heating the cyanides may be dissolved in HNO, Aq, the solution evaporated to dryness. and the residue strongly heated By now treat ing with cone HClAq, CuO is dissolved away, while Pd remains -2 NH Cl is added to the solution in aqua regia, and the liquid is filtered from PtCl, 2KCl, the filtrate may contain Ir, Rh, Ru, some Pt and Cu, besides Pd These metals are ppd by addition of Zn or Fe pp is treated in various ways Wilm (B 15, 241, v also B 13, 1198, 14, 629) recommends to dissolve the ppd metals in aqua regia, to boil the solution with excess of NaOHAq (von Schneider, A Suppl 5, 261), whereby the perchlorides of the metals, except that of Pt, are reduced to the lower chlorides, to acidify with HClAq, and add excess of NH₄Cl, in order to ppt PtCl, 2KCl The filtrate from this pp. 1s boiled with excess of NH,Aq, filtered, and excess of HClAq is added. After some time yellow pp. forms, which is either almost pure PdCl, 2NH, Cl, or if somewhat dirty-yellow in colour, it may contain Rh.Cl. 10NH. This pp is treated with contain Rh₂Ol₂.10NH₂ This pp is treated with cold NH₂Aq, in which the Rh salt is insoluble, and pure PdCl2.2NH4Cl is ppd by adding HClAq to the solution The pp is collected, washed with absolute alcohol, dried, and heated strongly: a grey spongy mass of Pd is obtained

This process may be used for purifying com-me coal Pd

For other m sthods of preparing Pd v Bunsen (A 146, 265), Philipp (D P J 220, 95), Guyard (C R 56, 1177), Rössler (Z 1866 175), Opificus (D P J 224, 414)

Pd may be prepared from palladium containing gold by dissolving in aqua regra, ppg with HgOy₂Aq, and proceeding as described under 1 abo?e Or the ore may be fused with an equal weight of Ag and some KNO, the regulus granulated, and treated with HNO, Aq (Cock, P M [2] 23, 16), Ag ppd by addition of NaCl, and Pd ppd with other metals by Zn, the Pd may then be separated from this pp as described under 2 above

Properties - As prepared by heating PdCl, 2KCl or PdCy, or by ppn from solutions, Pd forms a grey metallic sponge which can be pressed together, more easily than Pt, to a compact mass This compact form is also obtained by melting spongy Pd, Pd is a white metal, fairly malleable, ductile, and hard (somewhat softer than Pt) Compact Pd may be polished softer than Pt) Compact Pd may be polished highly, it can be hammered into thin plates, and drawn into fine wire In Brazilian gold ore Pd is found in regular octahedra, and in specimens of ore from the Harz it forms hexagonal plates Joly (N 43, 541) obtained it in cubic octahedra by dusting Pd ribbon with powdered topaz and heating to bright redness for some time by an electric current Heated in the OH flame to c. 2000°, Pd volatilises in greenish vapours, and condenses again to a brownish sublimate which is a mixture of metal and oxide the metal is melted in presence of O it absorbs O, which it gives up again on cooling (Deville a. Debray, A Ch [3] 56, 385) When strongly heated in air Pd is oxidised superficially, but the film of oxide is reduced at a higher temperature Heated in an alcoholic flame, Pd black absorbs C and increases largely in volume Pd absorbs H, it causes the combination of H and O when brought into electrolytic gas Heated Pd foil brought into a mixture of NH, and O causes for-mation of NH, NO, and NO. Pd is more easily acted on by acids than any other of the Pt metals, it is dissolved by cold HNO, Aq

The at w has been determined by analysing PdCl₂2KCl (Berzelius, P 13, 455), and by estimating Pd in PdN₂H₄Cl₂, by reducing in H

(Keiser, Am 11, 398)

In its chemical relations Pd is closely allied to Ru and Rh, and less closely to Os, Ir, and Pt

(v Noble metals, this vol p 628)
On account of its silver-like appearance, and its resistance to the action of H.S. Pd is used for making scales and division-marks on scientific instruments, and also for coating and preserving silvered metallic ware Pd wire is used in dentistry, an alloy with steel is used in making parts of physical instruments, and an alloy with steel, Cu, and small quantities of Au, Ni, Pt, Rh, and Ag is used in watch-making, as it is non-oxidisable, hard, and non-magnetic. Finely divided Pd is used in gas analysis for absorbing H from mixtures, and for effecting

the gradual combination of H or hydrocarbons with O (Hempel, B 23, 636, 1006)

Reactions and Combinations -- 1 When Pd is heated in air or oxygen Pd₂O is formed, but this oxide is reduced to Pd and O at a higher temperature -2 Heated in hydrogen to c 100° much H is absorbed, probably with formation of a hydride Pd₂H (v Hydrogen, vol 11 p 720) -8 Brought into a mixture of hydrogen and oxygen, in the ratio 2HO, Pd black causes formation of H2O without explosion (Coquillon, C R 83, 709) -4 Heated with sulphur Pd.S 18 formed -5 PdSe is formed by heating Pd with selenion —6 Digested with bromine and water, PdBr₂ is produced —7 With sodine tracture PdL₂ 18 produced —8 Glowing Pd wire causes the decomposition of many hydrocarbons into C and H (Coquillon, C R 84, 1503, Wilm, B 14, 874) — 9 In an alcoholic flame Pd becomes covered with O, spongy Pd increases largely in volume, probably with formation of a carbide (Wöhler, A. 184, 128) -10 Heated Pd foil brought into a mixture of ammonia and oxygen causes formation of NH₄NO₂ and NO₂ without explosion (Kraut, B 20, 1118)—11 Pd is oxidised to PdSO, by fusion with potassium - hydrogen sulphate -12 Pd dissolves in acids more easily than any other of the Pt metals in mitric acid, even in the cold, it dissolves to Pd(NO,), in hydrochloric acid, especially when Cl is passed in, PdCl, is formed, in hydriodic acid, PdI, is produced, PdBr₂ is obtained by dissolving in hydrobromic acid, with a little HNO.Aq, in sulphuric acid, with a little HNO, Aq, PdSO, 18 produced, Pd dissolves in aqua regia to form PdCl, PdCl, being perhaps produced at first

Qualitative discrimination between palladium and platinum If a drop of an alcoholic solu tion of I is dropped on to Pd, a black stain of PdI₂ is formed, and this stain disappears on heating, as Pt is not acted on by I tincture, this reaction serves to distinguish between the two

metals

Palladium, alloys of Alloys of Pd with eral metals have been prepared. The alloy several metals have been prepared formed by heating equal weights of Pd and lead, and removing the excess of Pb, is a steel-grey powder, S G 11 255, agreeing in composition with the formula Pd.Pb (Bauer, B 4, 451) Tin forms an alloy which seems to be a compound Pd, Sn, (Deville a. Debray, A Ch [3] 56, 885) Alloys with Sb, As, Ba, Bi, Cu, Au, Hg, N1, Pt, and Ag have been described (v Graham, C R 68, 1511, Mallet, C N 46, 216, Fischer,

8 51, 197

Palladium, ammonio-salts of, or Pallad-am-(Palladamines Ammoniacal monium salts palladrum bases) When HClAq is added to PdCl₂Aq containing an excess of NH₂, the salt PdCl₂2NH₃ separates, by treatment with Ag₂O and H₂O, this salt gives the strongly alkaline base Pd(OH), 2NH, and by neutralising this base with acids various salts are obtained, eg PdSO, 2NH,, PdCO, 2NH,, &c When a large excess of NH, is added to PdCl, Aq and the solution is evaporated, or when a solution of PdCl-2NH, in NHAq is evaporated, the salt PdCl_4NH, separates Similarly, when PdSO, is dissolved in a large excess of NH,Aq, the salt PdSO 4NH, is obtained by evaporating this solution; decomposition of the sulphate with BaOAq, and evaporation, gives the strongly alkaline base Pd(OH)₂ 4NH₃, which yields salts by neutralisation with acids, e g PdCO₃ 4NH₃, PdCO₄ 4NH₄, PdSO₄ 4NH₃, &c The compounds Pd(OH)₂ 2NH₄ and Pd(OH)₂ 4NH₄ represent the two series of palladium ammonio-salts The reactions of these compounds and their derivatives lead to their representation as, in one case, compounds of the radicle PdN₂H₆—derived from N.H. by replacing 2H by Pd-and, in the other case, compounds of the radicle PdN H12-derived from PdN₂H₆ by replacing 2H by 2NH₄ The two series of salts may be called pallados drammonium compounds, Pd(NH, NH,)Cl2, &c , and ammonium pallados diammonium com pounds, Pd(NH₂NH₄NH₄NH₄)Cl₂, &c The mem-bers of the first series are also sometimes called palladosamine compounds, and those of the It is second series pallado diamine compounds to be observed that both series are obtained from palladosochloride, PdCl₂ (cf IRIDIUM AMMONIO-SALTS, this vol p 47) The palladium ammonio salts have been examined chiefly by Kane (T 1842 275), Fehling (P 13, 466), Fischer (P 71, 431), and Hugo Müller (A 86, 341)

I PALLADOS DIAMMONIUM COMPOUNDS

 $N_2H_0Pd X_2^1$, or $(NH_3 NH_3)Pd X_2^1$, or perhaps

NH2(NH4)Pd X12

Pallados-diammonium chloride, N.H.Pd Cl. (simplest formula PdCl, 2NH, = di ammoniopalladium dichloride) This salt is known in two forms 1 Yellow crystals are obtained by adding HClAq to PdCl2 in excess of NH2Aq, these crystals are scarcely sol water, sol with difficulty in cold acids, more sol hot acids, easily sol NH3Aq, from which solution acids reppt the salt unchanged The salt dissolves in KOHAq, but no NH, is evolved even on heating, when the salt is suspended in water and Cl is passed in, solution is effected, addition of NH,Aq now ppts the red form of the salt, and boiling with KOHAq evolves NH, and leaves a liquid from which crystals of PdCl₂2NH₄Cl separate The continued passage of Cl produces PdCl, 2NH,Cl, and finally PdCl,Aq 2 A red salt of the same composition is obtained by dissolving the yellow salt in cone HClAq and adding NH,Aq, also by adding a slight excess of NH, Aq to a rather dilute cold solution of PdCl2Aq The yellow salt is produced by dissolving the red variety in NH₃Aq and adding excess of HClAq, also by heating the red salt to 200° Jorgensen (Gm K 3, 1242) regarded the red salt as polymeric with the yellow, and gave it the formula Pd(NH, NH,),2Cl, Cl,2Pd The salts may be isomeric, one being Pd NH,Cl NH,Cl and the other Pd NH2Cl2 NH4

Pallados-diammonium hydroxide,

N₂H₂Pd₄(OH)₂ (simplest formula Pd(OH)₂.2NH₄ = di ammonio palladium hydroxide) This base is obtained by decomposing the corresponding chloride with moist Ag₂O in presence of water, or the sulphate with BaOAq, the solution thus obtained is yellowish, odourless, and has a strongly alkaline taste and reaction. The base is obtained as a circly crystalline mass by eva porating at the ordinary temperature in absence of air. The solid rapidly absorbs CO₂ from the air, forming N₂H₂Pd CO₂, it is decomposed by heating to somewhat above 100°. The base is sol. water, the solution decomposes NH, salts.

and ppts CuO,H₂ and Ag₂O from solutions of salts of Cu and Ag The solution may be boiled with very slight change, on boiling with alco hol, Pd is ppd The other salts of this series which have been described are as follows M=PdN,H₄ — bromide MBr₂, carbonate MGO₃, fluoride MF₂(?), volide MI₂, nitrate M(NO₃)₂, mutrite M(NO₃)₂, sulphate MSO₄, and sulphite MSO₄

II AMMONIUM PALLADOS DIAMMONIUM COM POUNDS N₂H₄(NH₄)₂PdX¹₂, or perhaps

(NH, NH,),Pd X1,

Ammonium pallados diammonium chloride Pd(NH₂NH₃)₂Cl₂, (or Pd(NH₃NH₃Cl)₂=pal lado diamine chloride, simplest formula PdCl₂4NH₃= tetrammonio palladium dichloride) This salt is obtained in large, colourless, monoclinic prisms, with one molecule of water of crystallisation, by evaporating a solution of yellow N₂H₂Pd Cl₂ with excess of NH₃, or a solution of PdCl₂ in considerable excess of NH₄Aq Heating the salt to 120°, or adding acid to a solution of the salt, causes formation of yellow N₂H₂Pd Cl₂. Addition of PdCl₂ to a solution of the salt causes ppn of flesh red Pd(NH₂NH₄)₂Cl₂PdCl₄ (Kane, Fehling) Treat ment of Pd(NH₂NH₄)₂Cl₂ with NH₄Cl and aquaregua is said to produce Pd(NH₂NH₄)₂Cl₂PdCl₄ (Croft, C N 16, 53)

Ammonium pallados diammonium hydroxide Pd(NH₂ NH₄)₂(OH)₂, (or Pd(NH₂ NH₃)₂(OH)₂ = pallado diamine hydroxide, simplest formula Pd(OH), 4NH, = tetrammemio palladium dichlor Obtained as a crystalline mass by decom posing a solution in water of the sulphate Pd(NH₂NH₄)₂SO₄ H₂O₅ produced by adding large excess of NH,Aq to PdSO,Aq and evaporating with BaOAq, filtering and evaporating The solution is odourless, it is strongly alkaline, and ppts hydroxides from solutions of salts of Al, Co, Cu, Fe, and Ni, but not from salts of Ag, it sets NH₃ free from NH₂ClAq The solution absorbs CO₂ from the air, it is decomposed by boiling with organic matter. If this base is neutralised exactly by acids, salts of the base are obtained, e.g. Pd(NH₂NH₁)₂CO₂, Pd(NH₂NH₄)₂SO₃, &c , excess of acid, especially of a haloid acid, causes decomposition into a pallados diammonium salt and a salt of NH_4 , eg $Pd(NH_2NH_4)_2(OH)_2 + 4HClAq = <math>PdN_2H_4$ $Cl_2 + 2NH_4ClAq + 2H_2O$ The other salts of this series which have been described $M = Pd(NH_2 NH_4)_2$ —bromide are as follows MBr, and the double compound MBr, PdBr, carbonate MCO₂, fluoride MF₂ (?), iodide MI₂, nitrate M(NO₃), double nitrite M(NO₃), Pd(NO₃), silicofluoride MSiF₄ (?), sulphate MSO₄ H₂O, sulphite MSO.

The reactions of such substituted ammonias as NH₂Me, NH₂Et, and NH₂Ph on salts of Pd produce compounds analogous with the ammoniacal bases described above, eg pallados diethylammonium chloride N₂H₄Et₂Pd Cl₂, and pallados diethylammonium chloride N₂H₄Ph₂Pd Cl₂, have been described (Müller, 4.

86, 341).

The substitution of tri ethi larsine and tri-ethylphosphine for ammonia, in the reactions with Pd salts, produces compounds similar to the N-containing bases, e.g. pallados ditricthylphosphoneum chloride PaktaPd Cla

(Cahours a Gal, C R 70, 897), and pallados drivethylarsonium chloride As, Et, Pd Öl, (C a G, C R 71, 208)

Palladum, bromide of Only one bromide of Pd is known, and that has not been prepared

free from impurities

PALLADIUM DIBROMIDE PdBr₂ (Palladous or palladoso bromude) The brownish solid obtained by dissolving Pd in a mixture of HBrAq and HNO₃Aq, or digesting finely divided Pd with BrAq, and evaporating, probably has the composition PdBr₂, but it has not been obtained pure Double compounds of PdBr₂ with bromides of Ba, Mn, K, and Zn have been prepared, but not rully examined, by von Bonsdorff (P 19, 347, 431), the K salt, K₂PdBr₄, crystallises in thick rhombic forms (Joannis, C R 95, 295) Palladum, chlorides of Two chlorides of

Palladium, chlorides of Two chlorides of Pd have been isolated, PdCl and PdCl₂, a third, PdCl₃, is known in combination As none of these chlorides has been gasified, the formulæ are not necessarily molecular (v Palladium, Halloid compounds of, post) None of the chlorides has been formed by the direct union of

Pd and Cl

PALLADIUM DICHLORIDE PdCl₂ (Palladous or palladoso chloride) By dissolving Pd in HCIAq, Cl being passed into the liquid or a little HNO, being present, evaporating repeatedly with HClAq to remove HNO, and finally concentrating, red brown prismatic needles of PdCl₂ 2H₂O are obtained, at a moderate temperature H₂O is given off, and PdCl₂ remains as a black brown crystalline solid (Kane, T 1842 275, Bottger, P 106, 495) PdCl, is also ob tained, partly as a sublimate and partly as a garnet red crystalline residue, by heating Pd2S in PdCl₂ a stream of Cl (Schneider, P 141, 519) dissolves in water to form a dark red liquid, from which some oxychloride, PdxOyClz, separates on evaporation In water containing HCl, Pddl dissolves very readily The solution is dark brown, and on treatment with bases it gives salts of the form M12PdCl4-chlorpalladites (v infra), this solution may be supposed to con tain pallados chlorhydricacid H.PdCi,

Double salts, chlorpalladites
PdCl, 2MrCl or M-PdCl. These salts are obtained by the reaction of various oxides with
PdCl, in dilute HClAq, or by adding various

chlorides to conc PdCl2Aq

Ammonium palladium dichloride or Ammonium chlorpalladite PdCl, 2NH₄Cl or (NH₄),PdCl₄ Olive-green needles with a bronze coloured lustre, e sol water, insol conc alcohol When strongly heated gives residue of finely divided Pd Obtained by adding NH₄Cl to FdCl₂A₄ containing HCl (Kane, T 1842 275, Wilm, B 18, 1202)

Potassium palladium dichloride, or Potassium chlorpalladite PdCl₂2KCl or K.PdCl₄Colden yellow needles formed by adding KClAq to conc PdCl₄Aq. The crystals are quadratic prisms (Joannis, O. R. 95, 295), they are fairly solin cold water, and much more sol in hot water Alcohol ppts the salt from a hot conc aqueous solution. An aqueous solution boiled with alcohol or SO₂ gives a pp. of Pd., the dry salt is very slow₂ decomposed by heat to KCl and Pd, the decomposition is slow even in presence of oxalic and (Rossler, Z. 1866, 175), but rapid in a stream

of H The other chlorpalladites which have been described are PdCl₂ AlCl₃ 10H₄O (Welkow, B 7, 803), BaPdCl₄ (von Bonsdorff, P 19, 347, 341), BePdCl₄, 6H₄O (W, Ic), CdPdCl₄, CaPdCl₄, MgPdCl₄, MnPdCl₄, NiPdCl₄, ZnPdCl₄, Co₂Cl₅ 12NH₂ 2PdCl₂ (Gibbs, Am S [2] 37, 58), Co₂Cl₅ 10NH₂ 2PdCl₂ (Garstanjen, Gm K 3, 1254), PdCl₂ Hg₂Cl₂ 5NH₄Cl (Wilm, B 13, 1202)

PALLADIUM SUBCHLORIDE PdCl or Pd₂Cl₂ Small quantities of this chloride are said to be formed, as a dark reddish brown crystalline solid, when PdCl₂ is heated to redness, the chloride deliquesces in air, and always contains PdCl₂

and Pd (Kane, T 1842 275)

PALLADIUM TETRACHLORIDE PdCl. (Palladi or palladic chloride) This chloride probably exists in a solution of Pd in aqua regia, or of PdO₂ in cone HClAq, the compound has not been isolated As this solution yields salts of the form Mi₂PdCl₄ when treated with various metallic chlorides, it perhaps contains palladichlor hydric acid H₂PdCl₄

Double salts, chlorpalladates
PdCl, 2M'Cl or M'PdCl. These salts are formed
by adding metallic chlorides to a solution of Pd
in aqua regia, or of PdO, in cone HClAq, or to
a solution of PdCl, in HClAq into which Cl has
been passed, some of them are also produced by
passing Cl into a solution of the corresponding

chlorpalladite

Ammonium palladium tetrachloride or Am

monium chlorpalladate PdCl, 2NH,Cl or
(NH,),PdCl, A bright red pp obtained by add
ing NH,Cl to cone PdCl,Aq saturated with Cl or

treated with cone HNO,Aq S C 2418 (Topsos,
J 1870 393) Reduced with difficulty, treated
with NH,Aq, N is evolved and PdCl, 2NH, is

formed (H Muller, A 86, 341)

Potassium palladium tetrachloride or Potassium chlorpalladate PdCl, 2KCl or K, PdCl, A cinnabar red powder, consisting of small regular octahedra, S G 2 738, obtained by mixing KClAq with PdCl, Aq saturated with Cl, or with Pd in aqua regia, also formed by treating K, PdCl, Aq with Cl (Topsoe, J 1870 393, Croft, C N 16, 53) When the aqueous solution is treated with NH, Aq, N is evolved and K, PdCl, is formed

The other chlorpalladates which have been described are BePdCl, 8H₂O (Welkow, B 7, 38), MgPdCl, 6H₂O (Topsoe, J 1870 393), NiPdCl, 6H₂O (T, Ic), ZnPdCl, 6H₂O (T, Ic)

Palladium, cyanides of, and Double cyanides, v vol in p 343

Palladium, fluoride of, PdF. This compound is produced, according to Berzelius, by adding HFAq to cone Pd(NO₂)2Aq, it is described as a brown pp scarcely sol water or HFAq, and as forming double salts with alkali fluorides

Palladium, haloid compounds of The haloid compounds of Pd have not been at all fully investigated The following table presents the compositions of those which have been isolated—

PdX.	PdX_{\bullet}
PdCi,	PdCl.
PdBr, PdI.	in solution and combination
	PdF. PdCl. PdBr.

The compounds PdX₂ form double salts PdX₂2MX=M₂PdX₃, and PdCl₄ forms PdCl₄ 2MCl=M₂PdCl₄, the acids H₂PdCl₄ and

H.PdCl, probably exist in solution The chlorpalladates M.PdCl, are not very easily reduced, the chlorpalladites M.PdCl, are readily oxidised to chlorpalladites. None of the haloid com-pounds has been gasified, the formulæ are the simplest that express the composition, but they are not necessarily molecular PdBr, is formed by digesting together finely-powdered Pd and Br in presence of water PdCl, and PdCl, are easily soluble in water, PdF2, PdBr2, and PdI, are insoluble or but slightly soluble in water

Palladium, hydride of Pd absorbs H very A piece of Pd foil which has been freely strongly heated in vacuo absorbs 648 times its volume of H at 90°-97° When electrolytically ppd. Pd is used as the negative pole in the electrolysis of water, it absorbs 982 vols H The physical properties of Pd charged with H make it very probable that a definite compound is formed, and that this compound has the composition Pd.H (for details v Hydrogen, vol ii.

p 720

Palladium, hydroxide of, v. Palladium, saides and hydrated oxides of

Palladium, iodide of, PdI When KIAq 18 added to PdCl_Aq or Pd(NO₅)2Aq, an almost black pp of PdI₂ H₂O is obtained, which loses H₂O in vacuo (Lassaigne, J Chim med 11, 57) PdI₂ is scarcely sol water, alcohol, or ether, slightly sol HIAq, easily sol KIAq, from which solution dark-red deliquescent crystals of potassium iodpalladite, K2PdI, separate on concentration As PdI, is scarcely sol water, the ppn of this salt may be used in the quantitative estimation of I in presence of Cl and Br PdI is decomposed to Pd and I at somewhat above 350°, the last traces of I are not removed by heat alone, but by heating in H (Berzelius)
Palladium, oxides and hydrated oxides of

Three oxides have been isolated, Pd₂O, PdO, and PdO, another, Pd,O, intermediate between PdO and PdO₂, seems to exist PdO and PdO₂ seem to form hydrates, but the exact composi tion of these is not settled These oxides all react with acids to form salts corresponding with PdO, Pd₂O at the same time forming Pd, and PdO2 evolving O It is, however, possible that some salts may be obtained corresponding with All the oxides are reduced to Pd when strongly heated The examination of the oxides

of Pd is very incomplete

PALLADIUM SUBOXIDE Pd2O A black powder obtained by heating to low redness the pp formed by adding Na, CO, to solution of a salt of PdO (Kane, T 1842 276), or by heating Pd black in a stream of air (Wilm, B 15, 2225) Decomposed to Pd and O by heating to full redness, reduced by H at ordinary temperatures, reacts with acids to form salts of PdO with

separation of Pd.

PALLADIUM MONOXIDE PdO (Palladous oxide) A black powder, prepared by heating Pd(NO₂), or by very gently heating a Pd salt with K2CO. or Na₂CO₂, and washing the residue with water Reduced very easily by H (Wöhler, A 174, 160), gives Pd and O when heated to full redness Soluble in soids with difficulty, forming salts PdX $(X = SO_4, 2NO_8, CO_8, &c)$

Hydrated palladium monoxide dark-brown pp obtained by adding K.CO, or Na.CO. to solution of a salt of PdO was described

by Berzelius as PdO H₂O, but it may be a basic carbonate, heated to low redness this pp gives

Pd,0

PALLADIUM DIOXIDE PdO₂ (Pulladir oxide) A black powder, obtained by ppg PdCl,Aq or K,PdCl,Aq with excess of KOHAq, washing and boiling with water, and drying at 100°, also by the action of ozone on compounds of Pd, and by the decomposition of water using Pd as the positive pole (Wöhler, A 146, 875, Mailfert, C R 94, 860, 1186) At low red heat gives PdO and 0, and at a higher temperature all 0 is given off Treated with dilute HClAq, gives PdClAq and Cl, with cone HClAq probably forms PdCl, No corresponding salts have been isolated with certainty

Hydrated palladium dioxide pp obtained by adding excess of KOHAq to PdCl,Aq or K,PdCl,Aq is probably PdO, xH,O, but the exact composition of this pp is not

known

Pallado Palladio oxide Pd.O. = 4PdO PdO. According to Schneider (P 141, 519), an oxide of this composition is obtained by melting K2PdS2 or Na.PdS, with KNO, and KOH, wash ing with water, and treating the residue with aqua regia It is described as a dull brown powder, which gives off all its O when heated to redness in air, and is reduced by H at the ordi-

nary temperature

Palladium, salts of. Compounds obtained by replacing hydrogen of acids by Pd All the salts of Pd which have been isolated with certainty correspond with the oxide PdO, the salts of Pd are generally obtained by dissolving Pd in the various acids, with a little HNO,Aq added, or in some cases by double decomposition from PdCl₂Aq or Pd(NO₂)₂Aq Only a very few salts have been examined, besides the salts of the haloid acids, the carbonate, nitrate, nitrite, sulphate, and sulphite have been isolated (v CARBONATES &c) PdCl4, corresponding with PdO₂, probably exists in solution, and several compounds of this salt—the chlorpalladates -have been obtained (v Palladium tetra-

chlorids, p 795)
Palladium, selenide of, PdSe A grey in fusible solid, resembling osm iridium, with which it is perhaps isomorphous (Rössler, A 180, 244), formed by heating together Pd and Se

(Berzelius)

Palladium, sulphides of Three sulphides are known, corresponding with the three oxides The highest sulphide, PdS, reacts with sulphides of more positive elements as a sulphanhydride,

forming sulpho-palladates M2PdS,

PALLADIUM SUBSULPHIDE Pd.S hard solid, SG 7803 at 15° Prep red by fusing together, for 15-20 minutes over a blowpipe, 100 parts yellow N₂H₄Pd Cl₂ (p 794), or 5 parts PdS, with 6 parts dry K₂CO₂ or Na₂CO₃, 6 parts S, and 8 parts NH,Cl, the fused mass is treated with water, and the lustrous blueviolet crystals of K.Pd.S., which are mixed with the Pd.S., are removed by agitating with water Pd.S is very stable, it is not acted on by acids, scarcely by aqua regia, melts at a red heat without change, loses S slowly when very strongly heated (Schneider, P 141, 519)

PALLADIUM MONOSULPHIDE PdS (Palladous sulphide). Obtained by heating Pd, or certain

Pd salts, with S, also by ppg a salt of PdO by From palm kernels an oil is obtained containing Prepared in the dry way, PdS forms a blue white, lustrous, metal-like, very hard solid, prepared in the wet way, it is a black powder Heated in air, slowly oxidises to a basic sulphate, heated in Cl forms PdCl, and S,Cl. (Fellenberg, P 50, 65) A colloidal soluble form of PdS was obtained by Winssinger (BI [2] 49, 452) by ppg from an extremely dilute solution and dialysing

PALLADIUM DISULPHIDE PdS, (Palladic sulphide) A dark-brown powder, scarcely acted on by HNO, Aq soluble aqua regra without separation of S (Schneider, P 141, 519), heated in a stream of CO, forms PdS and then PdS Obtained by decomposing solution of a sulphopalladate by dilute HClAq, and washing the

 $Na_{\bullet}PdS_{\bullet}Aq + 2HClAq = 2NaClAq + PdS_{\bullet} + H_{\bullet}S$ This sulphide reacts as an acid anhydride with the sulphides of several of the more positive metals

Sulphopalladates These salts belong to two series, M.PdS, and M.Pd.S. = M.PdS, Pd.S

(Schneider, P 141, 519, 148, 625)

Sodrum sulphopalladate Na, PdS, (Sodrumpalladrum sulphide) This salt has not been obtained pure, as prepared by fusing 1 part N.H.,Pd Cl. (p 794), or 5 part PdS, with 6 parts dry Na,CO,, and 6 parts S, to full redness, and washing the residue with water, it forms reddishbrown needles, which dissolve in water to form a brown liquid deconsposed by HClAq with ppn of PdS.

Silver sulphopalladate Ag.PdS. A black brown powder obtained by adding the Na salt to

an alcoholic solution of AgNO,

The members of the other series of sulphopalladates, M.Pd.S., may be looked on as double compounds of M.PdS, and Pd.S., or as the salts of a hypothetical sulphopalladic acid H.Pd.S. These salts may perhaps be termed meta sul-

phopalladates

Potassum meta-sulphopalladate, K.Pd.S., or K.PdS.,Pd.S. Formed by melting 2 parts N.H.Pd Cl. (p 794), or 1 part PdS, with 12 parts K.CO., and 12 parts S, at a red heat, and wash ing the fused mass with water (Schneider, P 141, 519) Six sided, blue-violet, metal like crystals, insol water, treated with HClAq, K is removed but no H₂S is evolved, and the crystals become steel-grey, perhaps H.Pd.S. may be formed, but if so this soon decomposes, and a sulphide, said to be Pd.S., remains (Schneider, P 141, 625) Another compound, which may perhaps be K,PdS, (corresponding with the hypothetical acid Pd(SH),) is formed, along with Pd, by heating in H Silver meta-sulphopallada

meta-sulphopalladate Ag.Pd.S. or Ag.PdS, Pd.S A white-grey, lustrous, crystal-line pp obtained by treating the K salt with an

alcoholic solution of AgNO

Palladium, sulphocyanides of, w vol ii.p 350 Palladium, thio- salts of, v. Sulphopalladates under Palladrum, sulphides of, supra

Extracted from the fruit of PALM 9IL, Elæis gumeensis Soft orange mass containing paimitic and cleic soids and their glycerides (Pelouze a. Boudet, A 29, 42, Guibourt, J. Chem Med. 1, 177, Henry, J. Ph. 51, 241).

the glycerides of oleic, stearic, palmitic, myristic. lauric, decoic, octoic, and hexoic acids (Oudemans, J pr [2] 2, 898)
PALMELLIN A

substance resembling hamoglobin, which occurs in Palmella cruenta a red fungus (Phipson, C R 89, 316, 1078, C N.

41, 216)

PALMITIC ACID C₁₆H₁₆O₁. [60 75°] (Reissert, B 23, 2243) Mol (271 5° 1 V at 100 mm) (Krafft, B 12, 1670, 16, 1721) (839°-356°) (Carnelley a. Williams, B 12, 1360) SG. (liquid) 42 853 S (alcohol) 9 2 at 19 5° (C a. HC (solid) 2,871,788 (Louguinine, A Ch [6] 11, 223) Occurs as glyceride in a very large number of animal and vegetable fats and fixed oils (Chevreul, Recherches sur les corps gras, Fremy, A 36, 44, Stenhouse, A 36, 50, Sthamer a Meyer, A 43, 335, Schwarz, A 60,69, Heintz, 480, 299, 88, 298, 92, 291, von Böck, J pr.
49, 295, Berthelot, A Ch [3] 41, 216, 432, 47,
297, Maskelyne, C J 8, 1) Its myricyl ether occurs in bees wax (Brodie, A 71, 150), and in human fat (Heintz), and its cetyl ether in sper-maceti (L Smith, A 42, 241) Occasionally occurs in the free state, as in palm oil, and in Lycopodium spores (Langer, Ar Ph [3] 27, 625)

Formation -1 By saponification of palmitin, spermaceti, and melissin -2 By heating cetyl alcohol with potash lime (Dumas a Stae, A Ch [2] 73, 113) -3 Together with acetic acid by fusing oleic or elaidic acid with potash (Var rentrapp, A 35, 209) -4 By saponifying birdlime with alcoholic potash (Divers a. Kawakita, C J 58, 271) -5 By saponifying the wax of Myrica cerifera (Chittenden a Smith, Am 6,

Preparation —1 Japanese wax (3 pts) is saponified with KOH (1 pt) and water (1 pt), the solution ppd by HClAq, and the acid rectified in vacuo (Krafft, B 21, 2265) -2 The fatty acids obtained by saponifying fats are dissolved in alcohol, and fractionally ppd with an alcoholic solution of lead acetate or a conc aqueous solution of barium or magnesium acetate (v. vol 1 p 56)

Properties - Small hard crystals (from alcohol), insol water, v sol boiling alcohol and Slightly decomposed on distillation. ether Chlorination, in presence of SbCl_s, yields CCl_s, C.Cl_s, and C.Cl_s [224°] (Hartmann, B 24, 1018). Oxidation by alkaline KMnO_s yields oxalic, such cinic, adipic, acetic, butyric, hexoic, oxyvaleric, and doxypalmite acids (Gröger, M 8, 486).

Oxidation by nitric acid (S G 136) yields succinic and glutaric acids (Carette, C R 102, 692)

The Ba salt distilled with NaOMe yields

pentadecane (Mai, B 22, 2133)

Salts -(NH,)HA', -KA' pearly scales (from alcohol), insol ether Dissolves in a small quantity of water, but a larger quantity ppts. KHA's, which crystallises from alcohol in pearly scales [100°] (Schwarz) — NaA' lamine. NaHA', Got by adding hot water (1500 pts) to NaA' Insol water, v sol hot alcohol—BaA', S. (alcohol) 0035 at 20° Pearly crystalling Got by adding hot water (1500 pts) to Pearly crystalline powder — CaA', S (alcohol) 0103 at 20°,— MgA', [120°] (H) — PbA', [112°] Powder greenish blue powder —AgA' il. sol water Blackened by light. CuA's greenish blu phous, sl. sol water

Methyl ether MeA' [28°] (Berthelot)

Ethyl ether EtA' [24°] (Heintz)
Isoamyl ether C₅H₁₁A' [9°] (Berthelot),
[18.6°] (Duffy, C J 5, 314) Waxy
Octyl ether C₅H_{1.7}A' [8.5°] Formed from
the octyl alcohol of castor oil

Dodecyl ether C12H23A' [41°] (K.) [48°]

Tetradecyl ether C₁₄H₂₉A' Hexadecyl ether C₁₆H₃₁A' [54°] (Krafft, B 16, 3023) Probably identical with the cetyl ether C1eH21A' [49°], which is the chief component of spermaceti, from which it is prepared by crystallisation from boiling alcohol

Octadecyl ether C₁₈H_s,A' Ceryl ether C₂,H_{ss}A' [7 ,**A**′ [. [79°] The chief

constituent of poppy wax (Hesse, B 8, 639)

Myricyl ether C₅₀H₆₁A' [72°] The constituent of bees wax that is insoluble in alcohol (Brodie, A 71, 159)

Glyceryl derivatives or Palmitins v vol

1i p 621

Phenyl ether O.H.A'. [45°] mm) (Krafft a Burger, B 17, 1379) (250° at 15

p-Tolyl ether C,H,A' (258° at 15 [47°] mm)

Chloride C, H31 OCl [c 12°] (192 5° at

15 mm) (Krafft a Burger)

Amide C₁₅H₂₁ CONH₂ [107°] Formed by the action of NH₃ on the chloride or ether, and also by heating tetradecyl malonic amide (Carlet, Bl 1859, 175, Krafft a Stauffer, B 15, 1730, Hell a Jordanoff, B 24, 990

Antitide C, H, CONHPh [90 5°] (283° at 17 mm) Made by boiling palmitic acid with excess of aniline (Hell a Jordanoff, B 24, 943)

Silky needles (from alcohol), v e sol ether

Anhydride (C_{1e}H₃₁O)₂O [64°] (Villier, B.

9, 1932)

Netrale C₁₅H₃₁ CN [31°] (252° at 100 mm) SG \$\foating\$ 8186, \$\frac{199}{2}\$ 776 Formed by dis tilling the amide with \$P_O\$, (K a S), and also by heating eyano palmitic acid (H a J) Sixsided tables Reduced by alcohol and sodium to hexadecylamine (Krafft, B 22, 811)

References — DI BROMO PALMITIC ACID and

HEXADECOIC ACID

PALMITIC ALDEHYDE C16H2O (198° uncor at 22 mm) Prepared by distilling a mixture of calcium palmitate and calcium formate (Krafft, B 13, 1416, 16, 1714) Plates,

sl sol ether Combines with NaHSO,
Palmitic aldehyde C, H₂₂O [47°] S (alcohol) 64 at 16°, 12 at 78° S (ether) 16 at Got by oxidation of cetyl alcohol with chromic acid mixture (Fridau, A 83, 23, Doll-

fus, A 181, 287) Crystalline PALMITIN v GLYCERIN

PALMITOLIC ACID C16H28Or Mol w 252 [42°] Formed by the action of alcoholic potash at 180° on di bromo-palmitic acid (Schröder, A 148, 22) Silky needles (from alcohol), insol water, v sol ether Br forms C10H20Br2O2 and C16H28Br4O2. Furning nature acid oxidises it to suberic acid and suberic aldehyde -BaA AgA' amorphous powder blackened by light.

Reference -Bromo Palmitolic acid PALMITONE (C₁₅H₂₁),CO Di-pentadecyl ketone [83°] S G \$799, 120 794 Formed by distilling calcium or barium palmitate with lime (Piria, C R 34, 140, Maskelyne, C J 8, 1, Krafft, B 15, 1714) Got also by heating palmitic acid with P₂O₂ at 210° (Kipping, C J

57, 986). Silvery plates, v sol alcohol and benzene Does not unite with NaHSO, (Lim Silvery plates, v sol alcohol and behavior and superior of the state of the st

Formed, together with suberic acid and suberic aldehyde by the action of fuming HNO on palmitolic acid (Schröder, A 143, 85) (from alcohol), insol water, v sol ether -AgA' white pp, turned violet by light

PANAQUILONE Can H 42 O 15 Occurs in the root of Panax quinquefolius (Garrigues, A 90, 231) Amorphous powder, v sol water and alcohol, insol ether Has a bitter sweet taste Its solution is ppd by tannin H.SO, forms a purple solution from which water ppts panacone HClAq also O₁₉H₃₀O₇ (?) a crystalline powder forms CO.

ms CO₂ and panacone on heating **PANICOLE** C₁₂H₂₀O to C₁₂H₁₇, OMe [285°] A crystalline substance in oil of millet (Kassner HClAq at 160° Ar Ph [2] 25, 395, 26, 536)

forms MeCl and C12H18O [78°] PAPAIN v PROTEIDS

PAPAVERINE C20H21NO. i.e. C(OMe) CH C CH CH N

C(OMe) CH C-(ether) 4 at 10° Occurs in opium (Merck, A 66, 125, 73, 50, Anderson, T E 21, Pt 1, Hesse, A 153, 75, Suppl 8, 261, Z [2] 7, 641)

Preparation—1 The aqueous extract of opium is ppd with Na, Oo, the pp dissolved in

ether and shaken with dilute HOAc The acetic acid solution is ppd by NaOH The pp digested with oxalic acid solution yields crystalline papa verine oxalate It is better, however, to dis solve the pp in acetic acid, remove thebaine by tartaric acid, ppt the mother liquor with ammo nia, wash the pp with alcohol, and then treat with oxalic acid The oxalate is recrystallised from hot water, ppd by CaCl₂, the filtrate ppd by NH, and the papaverine recrystallised from alcohol (Hesse) -2 A solution of the hydro chlorides of the opium bases is ppd with conc NaOAc The pp, consisting of narcotine and papaverine, is dissolved in HClAq, and diluted till it contains only 25 pc of narcotine K.FeCy, is then added and, after 24 hours, the pp of papaverine ferricyanide is collected and decomposed by NaOHAq (Plugge, Ar Ph [8] 25, 343)

Properties -Trimetric prisms (from ether alcohol), abc = 32142 Narcotic Nearly insol hot water, v sol hot alcohol and chloroform, m sol hot benzene Cannot be sublimed Inactive to light (Goldschmiedt, M 9, 42) Conc H.SO, forms a colourless solution, becom ing dark violet on warming. On adding dilute H2SO4, HCl, or HNO, to a solution of papaverine in acetic acid, the sulphate, hydrochloride, or nitrate is ppd A solution of papaverine in conc H.SO, gives a pp of sulphate on adding water Papaverine is a weak base, its solutions do not affect litmus With ammonium selenite dis solved in conc H₂SO₄ it gives a bluish colour changing to red (Ferreira da Silva, *El* [3] 6,87, C R 112, 126)

Reactions -1. Potash-fusion yields methylamine, C.H.Me(OMe), [1 8 4], and protocatechnic acid (Goldschmiedt M 4,704, 6,969) —2 Yields McCl on heating with HClAq —3 Aqueous needles — (B'CH_Bz), PtCl. — B'CH_BzNO, 2aq KMnO, oxidises it to papaveric, veratric, m = (B'CH_Bz), Cr. O, and B'CH_BzO, H.N.O, hemipic, pyridine (a) tri carboxylic, dimethoxyconchonic, dimethoxy phthalic, and oxalic acids, hemipic iso imide NH₁, papaveraldine and CO₂. Papaveric acid (v infra) is the main product

(Goldschmiedt, M 6, 372, 8, 510)

Salts -B'HCl [220°] S 2 7 at 18° Large monoclinic crystals, a b c = 83 1 58, 6 = 92° 20′ (Foullon, M 6, 675) -B'₂H₂PtCl₂ 2aq [198°] — B'₂H₂ZnCl₄, white dimetric crystals, a c=1 84 — B'₂H₂Cl₂ZnI₂ plates (from alcohol)

— B'₂H₃CdCl₄ [176] — B'₄H₂Cl₂CdBr₂ [185°]

(Jahoda, M 7, 506) — B'H₂Cl₂CdI₄ [180°] — [21**4**°] B'2H2HgCl, triclinic prisms -B'HBr Monoclinic crystals, a b c = 831 58, $\beta = 92^{\circ}$ 60' —B'HI [200°] Monoclinic, sometimes isomorphous with the hydrochloride, but when crystallised from alcohol abc=181212, B=91° -B'HI Purple monoclinic prisms -B'HI. thin reddish needles -B',H,HgI, B'HNO, monoclinic tables, abc = 82155, $B = 94^{\circ}9' - B'H_2SO_4$ monoclinic prisms, a $b c = 83 \ 11 \ 38$, $\beta = 92^{\circ} \ 29' - B'H_2Cr_2O_7$, Flat orange needles $-B'H_2C_2O_4$ 8 26 at 10° Prisms -B'C_eH₂N₂O, [179°] Golden tables alcohol) - Succinate B'2C,H.O. [171°] -Benzoate B'C,H₂O₂ [145°] -Salicylate B'C H₂O₃ [130°] - Meconate B'C,H₄O, aq prisms, al sol alcohol—Ferro-cyahide B'₄H₄FeCy₆ (Plugge, Ar Ph [3] 25,

Methylo-vodide B'Mel 4aq Melts at 195° when anhydrous 55°-60° when hydrated Insol ether, sol water and alcohol Moist Ag₂O forms ether, sol water and alcohol Moist Ag₂O forms a caustic hydroxide, capable of giving a car bonate (Claus, J pr [2] 38, 496, Goldschmiedt, M 10, 673) The following compounds have been prepared from the methylo iodide (Stransky, M 9, 751) B'MeOH raq Melting at 215° when anhydrous, B'MeCl [75°], B'_Me PtCl_e 3aq, B'2Me2Cr2O [85°], and the picrate B'MeC8H2N2O,

[205°

Ethylo bromide B'EtBr 4aq [140°-145°] (Goldschmiedt, M 6, 667) or B'EtBraq [111°] (Claus a Huethn, B 18, 1576) Trimetric needles, a b c = 70 1 64 Boiling KOHAq forms the alkaline oxide (B'Et), O, sl sol cold water

Ethylo-chlorede B'EtCl 4aq

Olives B'Et,PtCl, 3\aq [223] [800]

Ethylo-rodide B'Etl [216°]

Ethylo-netrate B'EtNO, 3aq Prisms Ethylo chromate B', Et, Cr,O, [78°] [175°] Ethylo picrate B'EtC, H, N,O

Benzylo chlorede B'O,H,Cl7aq [165°] KMnO, oxidises it to veratric acid, benzylpapaveraldine, papaveraldine, and hemipic iso benzyl imide Aqueous (20 pc) KOH forms (B'C,H,),20 [165°] -B',2(C,H,),2PtCl, crystalline pp -B'O,H,C,H,N,0, [185°] -B',2(C,H,),2C,O,

o-Natro-bensylo-chlorade B'C, He(NO2)Cl Crystallises with 4aq, 6aq, and 9aq (Seutter, M 9, 859) — (B'C, H4(NO2)Cl)2PtCl4: crystalline pp —B'C,H_e(NO₂)NO₂ 1½aq prisms —
(B'C,H_e(NO₂))₂Cr₂O₇. yellow prisms —
B'C,H_e(NO₂) J_eH₂N₂O₇; yellow prisms (from alcohol)

Phenacylo-bromede B'CH2BzBr 21aq. Effiorescent pyramids (Seutter, M 9, 1085)
Forms the derivatives: B'OH,BzCl 6aq. yellow

[182°] An aqueous solution of the phenacylobromide gives with dilute NaOHAq a pp. B'CH2BzOH, whence boiling alcohol produces (B'CH₂Bz)₂O [186°], crystallising in colourless

Tetrahydride C₂₀H₂₅NO₄ [201°] by reducing papaverine with tin and HCl (Goldschmiedt, M 7, 497) Small prisms (from dilute alcohol), m sol hot water, sl sol ether B'HCl 8aq [290°] Monoclinic needles, with very bitter taste, causes albuminuma when injected internally - Salts B'2H2PtCle 3aq - $B'H_2SO_4$ 7aq $-B'H_2C_2O_4$ 6aq $-B'_2H_2Cr_2O_7$ $-B'C_4H_2N_2O_7$ [270°] Yellow needles, v sl sol alcohol

Bromo-papaverine C20H20BrNO4 Got by adding bromine-water to a solution of papaverine hydrochloride Monoclinic crystals, insol water, v sol alcohol and ether -B'HBr

Nitro papaverine $C_{20}H_{20}N_2O_6$ aq [163°] S (ether) 03 at 12° Made by boiling papaverine with dilute nitric acid (8 G 106) (Hesse, A. Suppl 8, 292) Pale yellow prisms (from dilute alcohol) Violently decomposes when quickly heated—Salts B'HCl 1½aq S 35 at 16°— B',H,PtCl,—B'HI v sl sol hot water— B'HNO, aq —B',H,SO, 8aq —B'H,C,O, 2aq yel low prisms, v sl sol water

C20H19NO Papaveraldine [210°] C₆H₅(OMe)₂·CO C₉H₄(OMe)₂N Made by oxidation of papaverine with KMnO, and dilute H.SO, (Goldschmiedt, M 6, 954, 7, Yellowish crystalline powder (from alcohol), insol water and alkalis, v sol hot HOAc H.SO, gives a red colour, changing to dark violet on warming Potash fusion splits it up into verstiic acid and dimethoxyisoquinol-Tin and HCl reduce it to papaverine lemon yellow tetrahydride — B'HNO, 2aq needles —B'HCl xaq yellow crystals, decom posed by water —B'.H.PtCl, aq orange prisms B'H.SO, —B'C,H,N,O, [209°] Methylo iodide B'Mel 3aq

Ethylo-bromids B'EtBr 3aq [above 270°] Bensylo-hydroxide B'C,H,OH or its anhydride (B'C,H,),O is a product of the oxida tion of paparerine benzylo chloride by dilute (2 p c) KMnO, at 45° (Goldschmiedt, M 9, 327) It crystallises from boiling water or alcohol in slender colourless needles [154°], converted by boiling HClAq into papaveraldine.

Oxim C₂₀H₁₀NO₄(NOH) needles, sol hot benzene [245°]. White

C20H19NO4(N2HPh) Phenyl-hydrazide Reddish yellow nodules (from alcohol)

Papaveroline C₁₆H₁₂NO₄ s c [4 3 1] C₆H₁(OH)₂,CH₂C₉H₄(OH)₂N Formed by boiling papaverine (3 pts) with HIAq (25 pts of SG 196) and red P for 10 hours (G, Krauss, M 11, 851) White crystalline powder (containing 2 aq), insol water, m sol alcohol, sl sol ether, w sol acids. Yields (a)-methyl-isoquinoline on distillation with zino-dust—Salts B'HCl white needles — B'₁H₂SO₄ S¹₂aq — B'HI 2aq — B'₂H₄C₄O₄ 3aq needles, m sol hot water

Papaveric acid C. H., NO, se C.H., (OMe), CO C.H., N(CO,H), [283°] Formed by oxidising papaverine with KMnO, (Gold-schmiedt, M 6, 890, 10, 158, 691). Minute

right-angled tables (containing aq), al sol water, alcohol, and ether, m. sol dilute alcohol Its solutions are acid in reaction Decomposes on fusion into CO₂ and pyropapaveric acid C_{1s}H_{1s}NO₃ [280°] Potash-fusion forms protocatechuic acid.

Salts - K2A" 23aq white leaflets, v e sol. Salvs — A₂A. 23ad white leaners, v e solvater — KHA" xaq needles — CaA" 1;aq — BaA" — Cu,A" (OH), 6aq — A₂A. 2;aq — AgH₂A", aq.—H₂A"HCl 2;aq · yellow needles Anhydrade. [170°]. Got by boiling papaweric and with Ac,O (Goldschmiedt, M 10, 159)

Mono-ethyl ether EtHA" [188°] Got by boiling the anhydride with alcohol Converted by NH, Aq into the amic soid

Oxim C10H12NO6(NOH) [c 156°] Small

needles (from alcohol) (Goldschmiedt, M 10, Phenyl-hydraside

Yellow needles (from dilute alcohol) [190°] Nitro-papaveric acid C₁₆H₁₂(NO₂)NO, [215°]

Formed by dissolving papaveric acid in conc HNO₂. Golden needles (containing aq) —Ag₂A" Pyropapaveric acid C₁₅H₁₃NO₃ [230°] Formed by fusing papaveric acid Minute white

leatlets — CaA", 4aq groups of needles —
BaA', 4aq — HA'HCl aq orange red needles — AgA' crystalline pp

Oxem C₁₅H₁₄N₂O₅ [226°] Nee alcohol) —B'HCl aq yellow needles [226°] Needles (from

Phényl-hydraside C₁₂H₁₈NO₄(N₂HPh) [228°] Yellow prisms —B'HCl

PAPAVEROSINE An alkaloid in dried poppy heads of Papaver somniferum (Deschamps, A Ch [4] 1, 453) Nacreous needles (from alcohol) Coloured red by H₂SO₄

PAPAYOTIN An amorphous hygroscopic powder ppd by adding alcohol to an aqueous extract of the juice of Carica papaya (Peckholt, Ph [3] 10, 343) It has an astringent, slightly sweet taste

PARABANIC ACID C.H.N.O. 10

co< Oxalyl urea Mol w 114 8 47 at 8° HC 212,700 H.F 2,200 (Matignon, C R 113, 198)

Formation -1 By dissolving uric acid (1 pt) in nitric acid (7 pts of SG. 13) at 70° and evaporating to a syrup, when parabanic acid crystallises out on cooling (Liebig a Wöhler, A 26, 285, Menschutkin, A 172, 74) —2 By oxidation of alloxan -3 A product of the action of HOCl on guanine (Strecker, A 118, 156) 4 From uric acid by heating with MnO_2 and dilute H_2SO_4 (Wheeler, Bl [2] 7, 521) or with KNO₂ and H_2SO_4 (Gibbs, B 1, 841) —5 A product of the action of HCl and KClO, on uric acid (Laurent a Gerhardt, A Ch [3] 24, 175)—6 By the action of POCl, on oxaluric acid NH₂CO NH CO CO₂H at 200° (Grimaux, C R 77, 1548) -7 By the action of PCl, on a mixture of oxalic acid and urea (Ponomareff, Bl [2] 18, 97) -8 By heating nitro-pyruvic ureide with bromine and water (Grimaux, C R 79, 1478) -9 By the action of Br and water on unc acid (Hardy, Bl [2] 1, 445, Magnier, Bl [2] 22, 56)

Properties .- Monoclinic laminæ (from water or alcohol); abc=1 665 478, $\beta=81^{\circ}$ 89'. Decomposed above 200°, forming a white sublimate Completely oxidised by KMnO, and H₂SO, to CO, and NH₂. Not attacked by HNO, in the cold. Its solution is not ppd by Ca salts,

but on boiling with alkalis it is split up into oxalic acid and ammonia In the same way lead salts and a little NH, give a pp of lead oxalate

(Maly, M 2, 284).

Reactions—1 In aqueous solution the salts rapidly change to exalurates -2 Zinc and MCl reduce it to oxalantin —8 Alcoholic NH at 100° forms oxaluramide —4 Alcoholic EtI at 100° forms C,H1,NO,I2 crystallising from alcohol in green prisms, nearly insol cold water (Hlasiwetz, A 103, 200) -5 Urea (1 pt) at 130° forms O.H.N.O., a sparingly-soluble powder (Grimaux, Bl [2] 32, 120)

Salts -NHA' Crystalline pawder, got by adding alcoholic ammonia to a solution of para banic acid in absolute alcohol Gives off its NH₃ at 100° Warm water converts it into ammonium oxalurate—NaA'—KA' Got by using alcoholic KOEt—AgA' Crystalline pp, got by adding AgNO, to a solution of KA'—
Ag,C,N,O, aq Got by ppg a solution of para
banic acid with AgNO, Insol water, sol
HNO,—Urea salt CON,H,HA' Four sided
tables, sl sol coldwater—Phenyl-hydrazine salt (N,H,Ph), A'aq [170°] Insol alcohol and ether Boiling water converts it into NH,CO NH CO CO N,H,Ph [215°] (Skinner a J 53, 550) -Aniline salt Ruhemann, O [250°] (S a R)

Hydrate C₃H₂N₂O₃ aq S 135 at 8° Formed from uric and (1 pt) and nitric and (3 pts of S G 13) at 60° The mixture is kept at 35°-55°, and finally heated to 70°, when the hydrate separates in large crystals (Tollens a Wagner, A 166, 321, 175, 227) Formed also by the action of POCl, on a mixture of urea and oxalic acid, heat not being applied (P) At 150°-160° it loses water and changes to ordinary

parabanic acid

CO NH CO Methyl parabanic acid

Methyl-oxalyl urea Oxalyl-methyl urea [149°] Formation —1 By heating nitroso creatinin with HCl at 100° (Dessaignes, A 97, 342, Marcker, A 133, 315)—2 From methyl uric acid and HNO₂ (Hill, B 9, 1093, 13, 739)—3 By the action of AgNO₂ on methyl thiopara banic acid (oxalyl methyl thio urea) (Andreasch, B 14, 1449, M 2, 279) -4 By oxidation of theobromine or caffoline with chromic acid mixture (E. Fischer, A. 215, 297, Maly a Hinteregger, B 14, 727, M 2, 94)

Properties - Colourless trimetric prisms, sol hot water Acid in reaction Not volatile with steam Decomposed by alkalis, even in the cold,

into methyl-urea and oxalic acid Salt —AgA' Needles, sol hot water

acid CO NMe CO Di methyl parabanic Oholestrophane [146°]. (276°) S 187 at 20°

Formation -1 The final product of the action of chlorine on caffeine in water (Roch leder, A 73, 128) —2 By boiling caffeine with nitric acid (Stenhouse, A 45, 871, 46, 229) — 8 By heating dry silver parabanate with MeI at 100° (Strecker, A. 118, 174) —4 By oxidation of caffeine with chromic acid mixture (Maly a Hinteregger, B 14, 723) -5 By the action of AgNO, on CS<NMe CO (Andreasch, M 2, 288) 6. By the action of dilute HClAq on murexoin (Brunn, B. 21, 515) —7. By passing ozonised oxygen through water in which caffeine is sus-

pended (Leipen, M 10, 184)

Properties — Trimetric prisms (from alcohol).

May be rublimed. Completely decomposed by alkalis dives no pp with lead acetate until allimonia is added, when lead oxalate is ppd Pure HNO, hay no action (Franchimont, R. T. O. 6, 217)

Reactions - 1 Alcoholic NH, forms dimethyl oxaluramide [225°] on heating HClAq at 200° splits it up into oxalic acid,
 CO₂, and methylamine (Calm, B 12, 624) —
 Cold alcoholic soda decomposes it into oxalic soid and di-methyl ures (M & H.) -4 Zinc and dilute $H_{\nu}SO_{\nu}$ reduce it to di-methyl-glyoxyl urea $CO < NMe \ CH \ OH$, a crystalline body, melting below 100°, decomposed by heating with baryta into glycollic acid, oxalic acid, methylamine, and CO₂ (Andreasch, M 3, 436) -5 On warming with water containing BaCO, it yields di-methyloxamide (Maly a Hinteregger, M 2, 88, 132)

Phenyl-parabanic acid CO NH CO [208°] Made from phenyl-urea and ClCO CO, Et (Stojentin, J pr [2] 32, 11) Silky plates, v sol alcohol, ether, and hot water

Di phenyl-parabanic acid CO NPh CO [204°] Formed by boiling an alcoholic solution of diphenyl guanidine dicyanide (dicyanomelaniline) C₁₃H₁₃N, or (a) tri phenyl-guanidine dicyanide with HClAq (Hofmann, Pr 11, 275, B 3, 764) Formed also by warming thiocarb anilido thio oxanilide with alcoholic AgNO, and by the action of ClCO CO.Et on di phenyl urea (Stojentin) Needles, insol water, v sol alcohol Decomposed by boiling KOHAq into oxalic acid, aniline, and CO. Yields with fum ing HNO, a di nitro di phenyl parabanic acid erystallising in needles

PARACONIC ACID v Lactone of OXYPYBO-TARTARIC ACID

PARAFFIN Solid, wax like, fatty mixture of hydrocarbons of the $C_nH_{2n+\frac{1}{2}}$ series, very rich in carbon and characterised by a very marked indifference to most reagents

Analysus -

85 15 849 85 5 85 31 84 86 14 85 14 31 14 44 15 02 149

1 Anderson, J 1857, 480, 2, 3 Brodie, P M [3] 33, 178, 4 Pawlewski, B 28, 327, 5 Gill a Meusel, C S J 6, 466 Beilstein states (Bn1, 139) that commercial paraffin usually contains 1 pc oxygen, which can be removed by heating with Na in a tube Lippmann a Hawliczek with Na in a tube Lippmann a Hawliczek (B 12, 69), from a sample of brown coal parafin v sl sol alcohol [87°] by heating with PCl₃, formed C₂H₄₀Cl₂, hence give formula C₂₂H₃₂. Bolley (A 106, 230), by heating hot parafin with Cl, formed C₂₂H₄₂Cl₄-Cl₂₂H₃₂Cl₁₃, hence gives formula C₂₂H₃₂Cl₃ Cl₃₂H₃₂Cl₁₃, hence formula C₂₂H₃₂Cl₃₄ Cl₃₄ Cl₃₅ Cl₃ gianual acetic and, finds $C_{11}H_{10}$ — $C_{11}H_{10}$, by dilute benser: and p xylene $C_{12}H_{10}$ — $C_{13}H_{11}$, and with saturated solutions in bensene and p-xylene Vot. III.

 $(C_{24}H_{so})_4-(C_{27}H_{so})_4$. It behaves as a colloid in most other solvents

Melting-point [45°-65°] By the action of solvents, small quantities of fractions [38°-45°] have also been obtained (Albrecht, D P J have also been obtained (Albrecht, D P 218, 280) Ozokerite paraffin [64°]

Bolling-point Above 800° In crude petroleum the portion (800°-400°) solidifies on cooling On fractionating, Bolley and Tuch-schmid found that the portion [53°] (300°) gave the following fractions (150°) [48°], (200°) [44 5°] and residue [53 5°]

Specific gravity varies from 0872-0912 at 17° (Albrecht) Ozokerite paraffin [64°] S G 20 0 917 [88°] S G 21 0 874 (Beilby, C J 43, 388) Paraffins expand considerably on melting

Occurrence — Occurs native as fossil wax, hatchettine, and ozokerite The latter is the most abundant, and is found in Galicia, Rou mania, on the island of Tscheleken on the east coast of the Caspian Sea, and on the island of Swjator at Baku When bleached it is called cerisine According to Zawziecki, ozokerite contains a crystalline and amorphous paraffin. It is also found in Etna lava to the extent of 43 pc in certain geodes (Silvestri, G 12, 9) It is obtained by the distillation of brown coal, turf, boghead coal, shales, schists, and natural bitumens, wood, wax, and wax and lime can also be obtained from brown coal tar Details of various methods are given by von Boyen, Z f Angew Chem 1891 261) Paraffin is also obtained in large quantities from American petroleum, being present in the high boiling portions which form a residue after the lighting oils have been distilled off Other mineral oils contain appreciable quantities of solid paraffin, eg Rangoon oil of Burma, 6 pc For the preparation of commercial paraffin from these bodies v Thorpe's Dictionary of Applied Che-MISTRY, and for a theory for its formation in nature by the decomposition of animal matter, vide Zawziecki, D P J 280, 69, 85, and 133

Properties - Paraffin, when pure, is a solid, colourless, translucent substance, perfectly in odorous and tasteless, somewhat resembling spermacet: It readily melts, forming a colour less oil, burns from a wick with a bright flame, but does not burn easily in the mass. It is insol water, sol hot alcohol, v sol ether and oils The solubility of paraffin from ozokerite has been studied by Pawlewski a Fillmonowicz (B 21, 2973), who show that the liquid con stituents are mostly sol glacial acetic acid, whereas vaseline, cerisine, ozokerite and paraffin are almost insoluble Pawlewski (B 23, 327) also states that ozokerite paraffin is sol formic acid, acetic acid, benzene, p xylene, and chloro-Thorpe a Young (A 165, 1), by heating form parafin in closed vessels at a high temperature, have resolved it into a little gas and hydrocarbons of the CaH2s series (CaH1e-C11H2), and others of the C_nH_{2n+2} series $(C_sH_{12}-C_{11}H_4)$ Higher solid and liquid hydrocarbons were also obtained Long heating at 150° causes an in crease of weight, attributed by Bolley and Tuchschmid to oxygen absorption $(Z \ 1868 \ 500$, Jaznnowitch, $B \ 8,768)$ Oxidised products can also be obtained by the action of oxidising agents Champion $(C \ R \ 75, 1576)$ has shown that nitrosulphume acid slowly transforms it at 90° into a liquid oil of the composition C₁₈H₂₆NO₅ (called paraffinic soid), from which ethereal salts have been obtained, and at the same time yields a white solid C₁₁H₂₂NO₆ sol Aq Fuming nitric acid, according to Pouchet, also acts upon paraffin at 110°, forming a true paraffinic acid C₂,H₄₈O₂ [46°] together with other fatty acids The acid has a wax-like odour, is insol water, but sol alcohol, ether, and benzene, is easily decomposed by heat, and forms deliquescent salts of the alkaline metals, and yellow, cheesy plates with the earths and magnesia. It is carbonised by sulphuric acid (Bl 28, 111, C R 79, 820) and nitric acid converts it into nitrocompounds and suberic acid Champion has also shown that chlorine is absorbed by paraffin in sunlight, producing hydrochloric soid cording to Gill a Meusel (Z 1869 65), CrO₃ and dilute HNO, oxidise paraffin to a mixture of cerotic $C_{27}H_{34}O_{27}$ succinic, and other fatty acids According to Beilstein a Wiegand (B 16, 1548), ozokerite contains a solid hydrocarbon of the olefine series It is formed by distilling the ozokerite in vacuo, and, after removing the first portions of only distillate, crystallising the solid portion from a solution of alcoholic benzene It is called *lekene* [79°] S G 0 9392, and is a very stable compound, being unacted upon by CrO, HNO, and KMnO, It is, however, com pletely oxidised by acid KMnO,, and slowly forms bromo-compound when heated with Br and H₂O m a sealed tube For methods of analysis of paraffin scale, and determination of impurities therein, vide B Redwood, S C I 3, 430, Journ Soc Arts, 1886 56, Sutherland, S C I 6, 123, 271, and Stuart Thomson, ibid 10, S R 342 et seg

PARAFFIN HYDROCARBONS v Hydro-

CARBONS

PARAFFIN OIL v PETROLEUM PARAGLOBIN v PROTEIDS PARAHEMOGLOBIN v HEMOGLOBIN PARALBUMIN v PROTEIDS, Appendix O PARALDEHYDE v ALDEHYDE

PARANILINE C₁₂H₁₄N₂ [192°] A base found by Hofmann (Pr 12, 314) in the prepara A base tion of crude aniline on a large scale silky needles (from dilute alcohol) EtI yields $C_{12}H_{12}EtN_2$ and $C_{12}H_{12}Et_2N_2 - B''_2H_2Cl_2$ aq six-

Bensoyl derivative C12H18BzN2 Needles

PARAPEPTONE v PROTEIDS

PARELLIC ACID C,H,O,? An acid sometimes obtained in the preparation of lecanoric acid (Schunck, A 54, 274) Needles (containing aq), v sl sol cold water, sol alcohol and ether Tastes bitter Reddens litmus -PbA', white flocculent p

PARICINE v CINCHONA BASES

PARIDIN Ca2H 56O14 S 15, S (alcohol) 2 A neutral glucoside extracted by alcohol from the leaves of Paris quadrifolia (Walz, Pharm Cont 1841 690, N Jahres Pharm 18, 174, Delfis, ibid 60,25) Formed also, together with a sugar, by boiling paristyphnin with dilute H₂SO. Thin lamins (containing 4aq) (from water) or tufts of needles (from alcohol) Conc H₂SO₄ turns it red Boiling HClAq decomposes

it, in alcoholic solution, into a sugar and re-

sinous paridol C₂H₄O₅

PARILLIN C₄H₄₆O₁₅ or C₄H₇₀O₁₅ [210°].

S 008 in the cold, 5 at 100° Ppd by adding water to an alcoholic extract of sarsar irilla root (Flückiger, Ph [8] 8, 488) Plates or prisms, sol hot alcohol and chloroform Cone H2SO4 gives a yellow solution Dilute I Cl gives green fluorescence and splits it up into a sugar and parigenin CmH42O4, which is insol boiling

PARISTYPHNIN An amorphous body which accompanies paridin, and may be ppd. by tannin Boiling dilute acids split it up into a sugar and paridin

PARPEVOLINE Name given to the hexahydride of di methyl ethyl pyridine, and to

pyridine bases isomeric therewith

PARSLEY The volatile oil of parsley con tains a terpene (162° 1 V), S G 12 865 (Gerichten, B 9, 259, Sauer a Grunling, A 208, 75). The seeds contain apiol $(q \ v)$ Water extracts

APIIN (q v) from the plant
PARSNEP The volatile oil of parsnep
seeds contains octyl n-butyrate (Renesse, A

166, 80)

PARVOLINE C.H. (c 200°) A product of the putrefaction of horse flesh (Gautier, Bl [2] 48, 11) Oil, smelling like hawthorn blos som, v sol alcohol and ether Resinifies in air Its platinochloride forms sparingly soluble fiesh coloured crystals

Parvoline C.H., N (~ 220°) A product of the distillation of cinchonine with potash (Oechsner de Coninck, C R 91, 296) — B',H,PtCl, brownish yellow powder

B',H,PtCl, brownish Parvoline C,H,,N (188°) A product of the dry distillation of the bituminous shale of

Dorsetshire (Greville Williams, C J 7, 97)
Parvoline C₀H₁₂N (188°) S G ²² 986 Got by distillation of coal (Thenius, J 1861 502)

Parvolines of known constitution v Di-ETHYL-PYRIDINE, DI METHYL-ETHYL PYRIDINE, TETRA METHYL PYRIDINF, and METHYL PROPYL-PYRIDINE

PASSIVE STATE OF METALS v Passivity

of iron, art IBON, p 52

PATCHOULI The volatile oil of patchouli, obtained from the leaves of Pogostemon Pat chouls, contains a sesquiterpene (which yields $C_{15}H_{24}$ 2HCl [118°]), and a camphor $C_{15}H_{26}O$ [55°], (296°), S G 4.5 1 051 (Gal, C R 68, 406, Montgolfier, C R 84, 88, B 10, 234, Wallach, A 238, 81). Patchouli camphor crystallises in hexagonal prisms, insol water, v sol alcohol and ether It is laworotatory $[a]_{D} = -118^{\circ}$ On distillation with ZnCl_{2} , or on heating with HOAc and Ac2O, it yields patchoulene C18H24

(254°), S.G. 2 946, [a]_p = -42°
PATELLARIC AGID C₁,H₂₀O₁₀ [above 100°]
Occurs in the lichen Patellaria (or Parmelia) scruposa, from which it can be extracted by ether (Knop, Weigelt, Z [2] 5, 298) Crystalline mass, insol water, v sol alcohol and ether Tastes bitter Decomposed on fusion or on boiling with baryta, with formation of orein and oxalic acid FeCl, gives a purple colour Cold baryta water forms a salt with transient blue

colour PAVIIN v FRAXIN.

RAN

PAYTIME C₁₁H₂₁N₂O. [156°]. [a]₀ = -49 5° in a 45 p.c. alcoholic solution An alkaloid extracted by alcohol from a white bark of an Aspidosperma from Payta in Peru (Hesse, A. 154, 287 \ 166, 259 \, 211, 280 \, Wulfsberg, Ph. [8] 11, 269 \, Arata, G 11, 246 \, O J 40, 622) Prisms (containing aq) sl sol water, sol ether, benzene, chloloform, and (unlike aspidospermne) ligroin Tastes bitter, is not poisonous When heated with soda-lime it yields paytone, a non mitrogenous substance Cone HNO, forms a colourless solution, changing through red to yellow FeCl₂ and cone H₂SO₄ give no colour Chloride of gold gives a purple pp 'HgCl₂ gives a yellow amorphous pp Bleaching powder produces, in an acid solution, a red colour changing through blue to yellow Salts—B'HCl S 6 at 15° Prisms—

Salts—B'HCl S 6 at 15° Prisms—B_H_PtCl, dark-yellow amorphous pp, dissolves in hot HClAq, forming a red solution changing to blue and depositing a blue pp

Paytamine C₂₁H₂₁N₂O An amorphous alka loid accompanying paytine Unlike paytine, KI does not ppt it from neutral solutions Its salts are amorphous, and it does not yield paytone

PECTOLACTIC ACID C.H.O. An acid got by boiling milk sugar with NaOHAq and less CuO than is needful for complete oxidation (Boedeker, A 100, 281) Brownish syrup, drying up to a varnish (containing 2\frac{1}{4}aq) Miscible with water and alcohol, insol ether Reduces ammoniacal AgNO, forming a mirror—BaA"4\frac{1}{4}aq powder, insol alcohol

PECTOUS SUBSTANCES Unripe fleshy fruits and fleshy roots (e g pears, carrots, and turnips) contain a substance (pectose) insolu ble in water, alcohol, and ether, transformed under the influence of acids into pectin, which is soluble in water, and is ppd as a jelly on adding alcohol or on boiling (Vauquelin, A Ch 5, 100, 6, 282, [2] 41, 46, Braconnot, A Ch [2] 28, 173, 30, 96, 47, 266, 72, 433, Guibourt, J Chim Med 1, 27, Mulder, J pr 16, 277, 16, 246, Fremy, A Ch [3] 24, 9, Soubeiran, J Ph [8] 11, 417, Poumarède a. Figuier, J Ph [3] 11, 458, 12, 81, Chodeff, A 51, 356, Scheibler, Z [2] 4, 433, Reichardt, Ar Ph [3] 10, 116, Giraud, C R 80, 477, Stude, A 131, 244, Rochleder, Z [2] 4, 381).

Pectin, obtained from the juice of ripe pears and apples by removing albuminoids by tannin

Pectin, obtained from the juice of ripe pears and apples by removing albuminoids by tannin and calcium by oxalic acid, and then ppg with alcohol, is, according to Bauer (J pr [2] 30, 370), a mixture of carbohydrates Different analyses of pectin give C 39 5 to 46 pc, H 55 pc, O 48 5-55 pc Pectous substances differ from cellulose in being stained by methylene blue, but, unlike lignin, the colour is destroyed by acids (Mangin, C R 109, 579) By boiling with water pectin is converted into 'parapectin,' a solution of which, unlike pectin, gives a pp with lead acetate Nitric acid yields mucic acid by oxidation. Boiling dilute acids convert pectin into 'metapectin,' which is acid in reaction and gives a pp with BaCl, (unlike pectin and parapectin). Boiling alkalis convert pectin into precious acid.

alkalis convert pectin into pectic acid

Pectic acid C₁₀H₂O₁, ? (Fremy) C 41 4 to
44 9 p c , H 4 71 to 5 4 , O 49 7 to 53 8 Got
by boing an aqueous extract of carrots with
Na₂CO₂ and ppg with HCl Produced also from

pectin in fruit by the action of a ferment (pectase) Jelly, drying up to a horny mass. Acid in taste and reaction, insol. cold water, alcohol, and ether. Converted by boiling water, first into parapectic acid and then into metapectic acid. Boiling dilute acids yield arabic acid.

and caller. Converted by boiling water, first into parapectic soid and then into metapectic soid Boiling dilute soids yield arabic acid Salts -Na₂C₁₄H₂₀O₁₄ -PbC₁₄H₂₀O₁₅.

Ag₂C₁₄H₂₀O₁₄ (Chodneff) -Ag₂C₁₄H₂₀O₁₅ (Fremy) Arabic acid, when prepared by hydrolysis of pectic soid, is called metapectic soid, and the arabinose got by the action of HClAq upon it is called pectinose Pectinose or arabinose is

tetra oxy-valeric aldehyde (q v)

References — Arabin and Cellulose

PELARGONIC ACID v ENNOIC ACID

PELLETIEBINE C.H.;NO (195°). S.G. 2 988 V D 4 88 (calc 4 66) S. 5 Occurs, together with methyl pelletierine, pseudo pelletierine, and isopelletierine in the bark of the pomegranate (Tanret, C R 86, 1270, 87, 358, 88, 716, 90, 695, J Ph [4] 28, 168, 384) It may be extracted from the powdered bark by shaking with chloroform and milk of lime If the chloroform is decanted and shaken with a dilute acid, the alkaloids will be taken up by the acid solution. The acid solution is mixed with NaOH and shaken with chloroform, which extracts pelletierine and pseudo pelletierine, which may be separated by crystallisation of their sulphates, the pelletierine is finally distilled in a current of H

Properties —Colourless liquid, partially decomposed at 195°, but may be distilled in vacuo. M sol water, miscible with alcohol, ether, and CHCl₂. The sulphate is lævorotatory; $[\alpha]_D = -30^\circ$ Resimined by absorption of oxygen. Fumes with HCl

Methyl pelletierine $C_9H_{17}NO$ (215°) 8 4 at 12° Extracted from an acid solution of the mixed bases by adding NaHCO, and shaking with chloroform Liquid, forming very deliquescent salts V sol alcohol, ether, and chloroform Its hydrochloride is dextrorotatory $[\alpha]_D = +22^\circ$

Pseudopelletierine C₂H₁₂NO [46°] (when hydrated) (246°) S 40 at 0° S (ether) 11 at 10° Crystallises from water in prisms (containing 2 aq), v e sol water, alcohol, and CHCl_Inactive as regards light Powerful base, expelling NH₂ from its salts. Gives the alkaloidal reactions Like pelletierine, it gives an intense green colour with H₂SO₄ and K₂Cr₂O₇ —B'HCl rhombohedra S 100 at 10° — B'₂H₂PtCl₆ needles —B'₂H₂SO₄ 4aq v sol water

Isopelletierine C.H., NO An inactive liquid, resembling pelletierine in other respects

PELOSINE C₁₈H₂₁NO, 1½aq An alkaloid contained in the root of Pareira brave or Cussampelos Pareira (Wiggers, A 27, 29, 38, 81, Bödeker, A 69, 53, Flückiger, N J. P. 31, 257) Extracted by dilute H₂SO₄, and ppd by Na₂CO₂, and dissolved in ether or CS₂. Amorphous powder, almost insol water Strongly alkaline in reaction Yields methylamine, dimethylamine, and a derivative of pyrrole on distilling with KOH (Williams, Chem Gas. 1858, 321)—B'HClaq amorphous —B'H,CrO,4aq. According to Flückiger, pelosine is identical with buxine and bebeerine

804 PELOSINE.

Pellute'in C, H, NO.? A yellow base, insol. ether, either formed from pelosine by atmospheric oxidation or occurring in Parewa —

PENDECANAPHTHENE or Pentadecanaphthene C₁₅H₅₀ (247° cor) SG ¹⁷ 829 Occurs in Russian petroleum (Markownikoff,

J R 15, 339) Liquid

PENNYROYAL The oil of pennyroyal from

Mentha pulegrum contains pulegone, which may be purified by fractional distillation in vacuo (Beckmann, A 262, 8, cf Kane, A 32, 286)

Pulegone Ci. H., O (131° at 60 mm) S G

29 382 [a]_D = +229° Somewhat viscid oil, smelling like peppermint Darkens in colour even in closed tubes. When reduced by Na it even in closed tubes When reduced by Na it gives 40 pc of menthol $-C_{10}H_{17}BrO$ [40 5°] [a]_p = -33 8° Made by passing HBr into $[a]_{p} = -33.8^{\circ}$ Made by passing HBr into pulegone dissolved in ligroin Whetstone shaped crystals v sol alcohol and ether This hydro bromide is converted by hydroxylamine into an oxim [38°] crystallising in four sided plates, which on standing lose Br and then melt at 110° This oxim also forms the hydrated oxim [157°] (v infra) by taking up water The hydrobromide is re-converted into pulegone by treatment with Ag₂O, while zinc-dust reduces it to pulegone hydride ($a = -174^{\circ}$), which yields an oxim [83°], and can be converted, by the action of Na on its ethereal solution, into lavorotatory menthol $[a]_D = -213^\circ$, giving a benzoyl derivative [54°

Hydrated oxem C₁₀H₁₈O(NOH) [157°] $[a]_{p} = -834^{\circ}$ in alcoholic solution Formed by the action of hydroxylamine on pulegone Long matted needles, sl sol ether, cold alcohol, and benzene Yıelds an acetyl derivative C_{1.}H_{1.}AcNO₂ [149°] and a benzoyl derivative [138°] —B'HCl 1189 $[a]_D = -324^\circ$ Trimetric crystals,

a b c = 605 1 1 048 -B'HBr [111°]
Pulegonamine C₁₀H₁₀NO Made Made by reducing the foregoing oxim with HI and P Amber coloured liquid, sl sol water, v sol alcohol and Tastes bitter Boiling MeI forms feNO Phenyl thiocarbimide forms ether C, H, MeNO PhNH CS N(C₁₀H₁₈O) [198°] Yields a benzoyl derivative C₁₀H₁₈BzNO [101°]—(C₁₀H₁₉NO)HCl [117°] Long needles, v sol water

PRNTADECANE C₁₁H₂₂ [10^o] (270°) (136° at 10 mm) S G ¹² 772, ¹² 769, ¹²⁰ 718 Made by reduction of C₁₃H₂₇ CCl₂ CH₃ or of pentadecoic acid with HI and P (Krafft, B 15, 1700) A pentadecane (114° at 15 mm) is ot by distilling barium palmitate with NaOMe (Mai, B 22, 2184)

(260°) S G — Pentadecane C18H22. Occurs in American petroleum when passed through red-hot tubes (Pelouze a

Cahours, Vohl, J 1865, 841)

PENTADECENOIC ACID C₁₅H₂₆O₂? Dtamenylvaleric acid (800°-806°) A product of the action of CO at 160° on a mixture of sodium isovalerate and NaOC, H11 (Geuther a Fröhlich, 4. 202, 804) Liquid.

PENTADECENYL ALCOHOL? C,,H,,O? [78°]. The portion of the wax of Frous gummeflua that is readily soluble in ether (Kessel, B 11, 2114). Nodules (from ether)

PENTADECINENE C, H (280°-240°) Got by heating the acetyl derivative of di-oxy-penta-

decane (triamylene acetate) with potash (Bauer,

A. 137, 249) Thick liquid. Unites with bromine. PENTADECOIC AGID C11H2002. [62°]. Formed by oxidation of cocceryl alcohol C_{so}H_{so}(OH); or of coccerns acid C_{st}F_sO_s with CrO, and acetic acid, the yield is about 40 pc. (Liebermann a Bergham, B 20, 964) Crystalline solid V sol alcohol, ether, acetic acid, and benzene, less readily in ligroin —A', Ca and A'₂Ba granular pps

Methyl ether A'Me. [68°], crystalline

solid Pentadecoic acid C₁₅H₁₀O₂ [51°] 100 mm) Made by oxidation of methyl penta decyl ketone with chromic acid mixture (Krafft, B 12, 1671, 19, 2983) Pearly scales -BaA'.

Pentadecoic acid C₁₅H₂₆O₂. [70°] Occurs, together with mannite, in the fungus Agaricus integer (Thörner, B 12, 1636) Small needles, w e sol ether and boiling alcohol, insol water

Isomerides v Cetic and Lactaric acid PENTADECONENE C15H28 (220°) Made from C15H2Br2 and alcoholic potash (Bauer, A 147, 255)

Pentadeconene (235°-245°) Made from santonic acid and HI (Cannizzaro a Amato, B 7,

DI PENTADECYL-CARBINOL

[85°] Made by reducing $(C_{15}H_{21})_2CH(OH)$ palmitone in boiling alcohol by adding sodium (Kipping, O J 57, 987) Silky needles or plates (from alcohol), sol ether, insol water With (from alcohol), sol ether, insol water With boiling Ac₂O it yields (C₁,H_{s1})₂CH O^Ac [49°], a granular powder, v sol ether

DI-PENTADECYL KETONE v PALMITONE n-PENTANE C.H. 1 e

CH, CH, CH, CH, CH, Mol w 72 (87°) SG 187 6282 (Schiff), 15 6337, 25 6250 (Perkin), $\mu_{\rm A}$ 1 3607 at 6 5°, $\mu_{\rm D} = 1$ 3649, $\mu_{\rm H} = 1$ 3769 (Gladstone, C J 59, 290) M M 5 638 at 17 2° Occurs in American and in Galician petroleum, in coal tar oil, and in resin oil (Greville Williams, C J 15, 130, Schorlemmer, C J 25, 1085, Pr 15, 131, Lachovitch, A 220, 190, Renard, A Ch [6] 1, 225) Oil. Yields on chlorination two amyl chlorides (106°) and (104°), and finally C₂H_aCl₄ (230°–240°) (Bauer, C R 51, 572, Schorlemmer, Lachovitch) CrO₂Cl, followed by water, yields OH2Ol CO C.H. (Etard) At a red heat it is decomposed with formation of ethylene, propylene, and butinene (Norton a. Andrews, Am 8, 1)

Isopentane (CH₂)₂CH CH₂ CH₂. Tri-methylane VD 250 (calc 248) (30°) SG 118 ethane 6248, 35 6159 (Perkin), 50.5 6132 (Schiff, A 220, 87), 48 6875 (Just, A 220, 153) SV 117 2 (Schiff) MM 5 750 at 16 4° Coours in Cours in American and in Galician petroleum (Warren, Z 1865, 668, Lachovitch) Formed by the action of water on zinc isoamyl, or by heating isoamyl iodide with zinc and water at 140° (Frankland, A 74, 47) It is also a product of the action of ZnCl₂ on hot isoamyl alcohol, and of zinc on

dry isoamyl iodide

The same pentane can be obtained from active amyl iodide by treatment, in alcoholic solution, with zinc and HOl in the cold (Just). Oil with characteristic odour, unlike 'ben_oline Not attacked by Br or HNO. Chlorine yields an amyl chloride (100°) Isopentane (1 c c) is oxidised by K₂Cr₂O₇ (4 g) and CrO₂ (20 g) in water (2000 c c) in five weeks at 15°-20° to iso-

valeric a nd (Berthelot, O R 79, 1435)

Pentane C(OH₃), Tetra-methyl-methane [e -20°]. (9 5°) H F p 47,850 H.F v 44,950 (Thomsen, 2.a.) Formed by the action of ZnMe, on tert-butyl fodde (Lwow, Z [2] 6, 520, 7, 257, Naumann, B 7, 173) Appears also to be formed from CH, CCl, CH, and ZnMe, (L) Oil

References -DI-BROMO , DI-GHLORO-, and IODO-

PENTANE

PENTANE CARBOXYLIC ACID v HEXOIC ACID

Pentane dicarboxylic acid v BUTYL MALONIC, ETHYL-GLUTARIC, DI ETHYL MALONIC, DI METHYL-GLUTARIC, PIMELIC, and PROPYL-SUCCINIC ACIDS

n Pentane tricarboxylic acid CPr(CO2H)2.CH2 CO2H [148°] Got by saponi-

fying its ether with alcoholic potash Slender needles, v sol water, alcohol, and ether up at 175° into CO₂ and propyl-sucoinic acid

Ethyl ether Et.A''' (280°) SG

Made from ethane tricarboxylic ether CO₂Et CH₂ CH(CO₂Et)₂, NaOEt, and PrI (Waltz, B 15, 608, A 214, 58) Oil, miscible with Oil, miscible with alcohol and ether

Mono-nitrile of the disthyl ether CPr(CN)(CO,Et) CH, CO,Et (205° at 45 mm) Formed from sodium cyano succinic ether and n-propyl rodide (Ba.the, Bl [8] 1, 305, C R

108, 297) Oil

Pentane tri-carboxylic acid. Ethyl ether C₂H₄ CH(CO₂Et) CMe(CO₂Et)₄. Methylbutenyl tracarboxylic ether (281 5° cor) SG 20 1 0575, μ_D 1 4847 at 20° Formed by the action of Na on a mixture of a bromo butyric ether and sodium methyl-malonic ether (Bischoff, B 22, 1817, 3180, 23, 647) Apparently the same acid ((281 8° cor), S G 49 10523, $\mu_{\rm D}=14340$ at 20°) is got from sodium butane tricarboxylic ether and Mel Both acids yield, on saponification by H₂SO₄, two methyl ethyl-succinic acids [88°] and [168°]

Pentane tri-carboxylic acid Ethyl ether C.H. $C(CO_2Et)_2$ CHMe CO_2Et (272 8° cor) S G 1 0609 μ_D 1 4874 at 20° Formed by the Formed by the action of Na on a mixture of a bromo propionic ether and sodium ethyl malonic ether (Bischoff The same, or an isomeric a. Mints, B 28, 648) ether (282 8° cor), S G Ψ 1 0607, $\mu_{\rm D} = 1$ 4373 at 20°) is got from sodium propane tricarboxylic ether and EtI Both acids yield, on saponification with H₂SO₄, methyl ethyl succinic acid [168°], the acid prepared by the second method yields also the isomeric acid [88°]

Pentane tri-carboxylic acid

CH₂(CO₂H) CH₂CH(CO₂H) CH₂CH₂CO₂H [7°] Formed from pentane tetra carboxylic ether by saponifying with alcoholic potash, and boiling the product with conc. HClAq (Emery, B 24, 284) Mass of needles —Ag, A''' white pp

Pentane tri-carboxylic acid C.H. CH(CO.H) CH(CO.H) CH.CO.H Made by the action of fumaric ether on sodium ethyl-malonic ether, the product being saponified (Auvers, B 24, 310) V sol. water and alcohol

Isopentane tri-carboxylic acid (OH_),OH.O(OO,H),-OH,-CO,H. [145°] (H1elt, B 16, 2622). Formed from its ether, which is

made from ethane tricarboxylic ether, NaOEt and PrI (Waltz, A 214, 60) Yields isopropyl succinic acid on fusion

Ethyl ether Et,A''' (270°-290°). Isopentane tri carboxylic acid

(CH₁)₂OH CH(CO₂H) CH(CO₂H)₂. Carbopimelie acid [160°] Got from its ether by cold alcoholic potash Monoclinic (?) crystals (from water), v sol water, alcohol, and ether composes on fusion into CO₂ and isopropyl-succinic (pimelic) scid.—Ba₂A'''₂ sticky pp Ethyl ether Et₂A''' (277°) Made from

a-bromo isovaleric ether and sodium-malonic ether (W Roser, A 220, 274) Liquid, with

bitter taste

scid Isopentane tricarboxylic ether CMe₂(CO₂Et) CMe(CO₂Et)₂. (284 3° cor) S G ² 10524 $\mu_{\rm p}$ = 14333 at 20° Made from sodium methyl malonic ether and a-bromo-iso-butyric ether (Bischoff a Mintz, B 23, 649) Made from Yields, on saponification by H.SO., tri-methylsuccinic acid [105°] and a small quantity of a substance melting between 108° and 122° The same, or an isomeric ether ((277 8° cor), 8 G 20 1 0575, $\mu_{\rm D}=1$ 4341 at 20°) is got from sodium isobutane tricarboxylic ether and MeI It yields, on saponification, tri-methyl succinic acid [105°] and u di methyl succinic acid [140°]

Pentane tetracarboxylic acid (CO2H)2CH CH2CH2CH2CH(CO2H)2 Oil, split up by heat into CO₂ and npimelic acid CO₂H CH₂CH₂CH₂CH₂CO₃H Ethyl ether Et₄A' (260° at 100 mm)

Got from sodium malonic ether and trimethylene bromide (Perkin, jun, C J 51, 241, B 18, 3248) Disodium salt CH₂(CH₂ CNa(CO₂Et)₂).
Amorphous powder, converted by bromine into pentamethylene tetracarboxylic ether

Pentane tetra-carboxylic acid CH₂(CMe(CO₂H)₂)₂. [164°] Got by boiling its ether with alcoholic potash (Dressel, A 256, 183) Crystalline mass, v sol. water, m sol. Converted by heating, by itself or in aqueous solution, into CH2(CHMe CO2H)2 [90°

Ethylether Et, A' (191° at 12 mm) Made by the action of MeI on a solution of di sodium propane tetra-carboxylic ether in alcohol

EthylPentane tetra-carboxylic acid ether C(CO,Et),(CH,CH,CO,Et), (215° at 13 mm) S G 20 1 1084 A by-product in the action of NaOEt on a mixture of \$-bromo-propionic ether with malonic ether (Emery, B 24, Colourless oil

PENTANE PHOSPHONIC ACID v ISOAMTL

PHOSPHINIC ACID

PENTANE SULPHONIC ACID C.H., SO.H. Formed by the action of nitric acid on isoamyl mercaptan, disulphide, or sulphocyanide (Gerathewohl, J. pr. 34, 447, Henry, jun, A. Ch. [8] 25, 246, Medlock, A. 69, 225) Deliquescent crystalline mass Chlorine acting on it in sunlight forms C.H., Cl.SO.H (Spring a. Winssinger, Bi [2] 41, 801) ICl, at 180° forms the same body, together with tri- and tetra- chloro-pent-

anes and C.H.CL(SO.H)
Salts.—BaA's (dried at 100°). Gyrates on water —PbA', waq colourless lamins — CuA', — AgA' plates Double salts with chloropentane sulphonates BaA'(O,H1,ClSO₃) aq.
—Ba,A',(O,H1,ClSO₃),Cl₂2aq

Ohloride C. H. SO. Cl. Liquid.

Pentane disulphonic acid CEt, (80,H). Frenche distriptions and Chi. (Co. 1).

Formed from COl. SO.H and ZnEt. in ether (lise, A 147, 145) Syrup—K.A" 2aq needles (from alcohol).—BaA" 2aq S 14 in the cold, e. 30 at 100°—PbA"—ZnA" 4aq plates

"PENTA-THIONIC ACIDS Thronic acids

under Sulphue, Oxyacids of, vol 1v **PENTATRIACONTANE C_s,H₇₂ [75°]. (381° at 15 mm) S G \$\frac{4}{3}\$ 7816, \$\frac{6}{2}\$ 777, \$\frac{10}{6}\$ **766. Formed by reduction of the dichloride of stearone with H and P (Krafft, B 15, 1715)

PENTENE v AMYLENE The name pentene is also given sometimes to pentamethenyl tri-

hydride

Dipentene v Terpenes

PENTENOIC ACID C.H.O. & e CHEt CH CO.H Propylidene acetic acid (196°) SG 19 988 Made by heating propionic alde-hyde with malonic acid, and HOAc at 100° (Komnenos, A 218, 166, Zincke a Kuster, B 22, 494) Oil—BaA's plates [270°]—CaA's aq nodules, v sol water and alcohol—CuA's green pp [91°] Yields Cu,O at 175°—AgA' bulky pp The same acid (SG 15 983) appears to be got by adding sodium-amalgam to an alkaline solution of CCl, CCl CCl CCl CO2H derived from pyrocatechin or o-amido phenol It combines with bromine.

Pentenoic acid CMe, CH CO, H Dimethyl-

acrylic acid [70°] (195) Formation —1 From CH₂Pr CO₂H by oxidising to CMe₄(OH) CH₂ CO₂H and heating the product with dilute H₂SO₄ (Neubauer, A 106, 62, W. von Miller, A 200, 261) —2 From-di methyl allyl-carbinol by oxidising to β -oxy-valeric acid and distilling this acid with dilute H_2SO_4 or treating its ether with PCl₂ (Semljanizin a Sayizeff, A 197, 72, Ustinoff, J pr [2] 34,478, Bl [2] 45,255)—3 A product of the action of alcoholic NaOEt on a bromo-isovaleric ether (Duvillier, C R 88, 913, 1209, 112, 1012, A Ch [5] 19, 428)—4 The chief product of the action of sodoform on sodium isobutylate (Gorboff, J pr. [2] 41, 228)

Properties — Monoclinic prisms, abc = 153.1 71, $\beta = 74^{\circ} 13'$ Sl sol water, v sol alcohol and ether Bromine combines, forming C₅H₅Br₂O₂ [108°] Converted into isobutylene

and CO, by heating for 30 hours at 220°
Salts — NaA' — BaA', 2aq groups of needles -CaA'₂.—CaA'₂4aq — ZnA'₂4aq —CuA'₂2aq —

PbA', aq -AgA'.

Isomerides -ALLYL ACETIC, ANGELIC, TETRA-METHYLENE CARBOXYLIC, and TIGLIC ACID

PENTENYL ALCOHOL C,H1,O & 6 CH. CHEt OH Vinyl-ethyl-carbinol. (114°). SG 8 856, 19 5 840 Formed from acrolein by successive treatment with ZnEt, and water (Wagner, J R 16, 319; B 21, 3349, Bl [2] 42, 330). Pungent liquid. Yields on oxidation by KMnO, propionic and formic acids, CO, and tri-oxy-pentane

Acetyl derivative C.H. OAc (182°) at 748 mm. S.G. § 913, $\frac{215}{6}$ 898 Liquid

Fentenyl alcohol CH. CH CH. CHMe OH

Methyl-allyl-carbinol. (116°) Formed by the action of since on a mixture of allyl iodide and acetic aldehyde (Wagner, B 21, 3850) on oxidation a tri-oxy-pentane, formic and acetic acids, and acetic aldehyde.

Pentenyl alcohol C,H10O Valerylens hy drate (115°-120°) Got by treating its acetyl derivative with solid KOH

Acetyl derivative C.H.OAc (735°). A product of the action of AgOAc on C.H.oCl. ob tained by combination of valerylene with HCl

(Reboul, Z 1867, 174)

Pentenyl alcohol CH, CH CH CMeH OH Methyl propenyl-carbinol (118°) Formed by the action of water on the corresponding pentenyl chloride, which is a product of chlorination of CHMe CHEt (Kondakoff, B 24, 931)

Pentenyl alcohol CH₂CH CMe₂-)H D₁methyl-vnyl carbinol Isoprenic alcohol (99°)
Formed from C₂H₂Cl, which is obtained from
soprene and HCl (Gradziatzky, Bl [2] 47, 168)
Smells like camphor Dilute H₂SO₄ at 109° forms a hydrocarbon

Acetyl derivative C, H,OAc (121°) A pentenyl alcohol (125°-135°) is a product of reduction of tiglic aldehyde (Lieben a Zeisel, M 7, 57)

References .- BROMO and CHLORO PENTENYL **ALCOHOL**

PENTENYL AMIDO-PHENYL MERCAPTAN

 $C_0H_4 < N > C CH_2 Pr$ Liquid, formed from o amido phenyl mercaptan and isovaleryl chloride

(Hofmann, B 13, 8, 1223) — B', H, PtOl, needles

PENTENYLAMINE O, H, N : e

CH, CH CH, CHMe NH, (85°) Got by redu oing nitro-amylene with zhic and HCl (Gal, J

1873, 333)

Pentenylamine C.H., NH. Valerylamine A product of the action of NH., on chloro amyl al cohol (amylene chlorhydrin) at 100° (Wurtz, 4 Suppl 7, 89) —B',H,PtCl, orange crystals PENTENYL BENZENE C,H, C,H, (178°-

177°) SG 84 Formed, together with a polymeride C₂₂H₂₈ (c 210°), SG ²³ 96, by boil polymeride $C_{22}H_{28}$ (c 210°), S G 23 96, by boiling bromo-amyl benzene C_4H_4 CHEt CHBr CH, with water (Dafert, M 4, 153, 616) Yields benz ore and acetic acids on oxidation

PENTENYL BROMIDE v BROMO-AMYLENE PENTENYL THIOCARBIMIDE C.H. NCS (190°) Formed from isoamylene bromide by successive treatment with alcoholic NH, and

CS₂ (Hofmann, B 12, 990) Liquid PENTENYL-THIO-UREA C,H,NH CS NH, [103°] Formed from pentenyl thiocarbimide and alcoholic NH, at 100° (Hofmann, B 12, 991)

PENTHIOPHENE The homologue of thio phene CH₂ CH CH OH S, known in some of its derivatives (Krekeler, B 19, 3270)

PENTIC ACID C.H.O. 10 CHEt CO. O? [128°]. A product of the action of alcoholic potash on bromo ethyl-acetoacetic ether (Demarçay, Bl [2] 27, 483, C. R 88, 126) Got also by heating bromo-ethyl-acetoacetic ether at 100° (Wedel, A 219, 104) Trimetric crystals, v sol. hot CHCl, Salts —NaA'aq —KA' aq: v. e. sol water

MgA', 5aq — CaA', aq — BaA', 2aq — ZnA', 5aq -MnA', 4aq

Ethyl ether CEt CO OH. O. Mol w 153 (obs by Raoult's method); (calc 156) (Moscheles a Cornelius, B. 21, 2607; 22, 244). Liquid. Phenyl - hydraside C.H.O.(N.HPh)

Crystals (from alcohol)

PENTINENES C.H. Pentylenes. Pentines. Mol w 68 Of the eight possible isomerides, three are derived from acetylene and precipitate ammoniacal silver and cuprous solutions, the remaining fige, so far as they are known, give no metallic derivatives The following are known

1 Propyl acetylene CH, CH, CH, C CH (48°-49°) Methyl propyl ketone by action of PCl, gives a dichloride, from which alcoholic potash withdraws 2HCl (Friedel, Z 1869, 124) Forms liquid dibromide (190°) and tetrabromide

(275°) (Bruylants, B 8, 411) 2 Isopropylacetylene (CH₂)₂CH C CH (28°-29°) The chloride from isovaleric aldehyde (Bruylants, B 8, 413) or isopropyl-ethylene bromide, is decomposed by alcoholic potash (Eltekow, Flawitzky, Krylow, B 10, 707 and 1102) Oxidised by chromic liquor into acetone, acetic, and isobutyric acids Bromides liquid, C₃H₅Br₂ (175°), C₃H₆Br₄ (275°) (Bruylants, B 8, 407) The silver compound C₃H₇Ag is white, dissolves slightly in ammoniacal silver nitrate solution, and crystallises therefrom in small prisms Converted by a solution KI into the compound C₄H₇I (140°) Converted by a solution of iodine in

3 Eltekow (B 10, 1904), by treating commercial amylene with sulphuric acid (dil with b vol H O) at 0°, obtained an insoluble amylene, the bromide of which, by the action of KHO, yielded a mixture of two hydrocarbons, of which one, the smaller amount (35°), gave a pp with ammoniacal silver solution. This he believed to be isopropylacetylene, though differing from

the compound described above in b p

4 Valerylene This name was given to the liquid (44°-46°) obtained by Reboul (A 131, 238) from the dibromide prepared from commercial amylene This substance is a mixture from which Eltekow obtained the hydrocarbon described under 3, and a larger quantity of another (51°-52°), which is stated (B 10, 2057) to yield acetic and propionic acids by treatment with chromic acid Hence Eltekow ascribes to it the formula, C₂H₃ C C CH₂, although it does not yield metallic derivatives Reboul's valeryl ene, heated to 250°-260°, yields a terpene C_{1e}H₁₆ (180°) (Bouchardat, Bl [2] 33, 24) Strong sulphuric acid converts it into a hydrate C_{1e}H_{1e} H₂O and polymerides C_{1e}H₂₁, &c (Reboul, A 143, 372) Yields a dibromide, which on A 143, 372) treatment with alcoholic potash gives C,H,Br, O.H. (valylene), and valerylene (Reboul, A 135, 372) Valerylene tetrabromide C.H.Br. is liquid. 5 Piperylene (42°) (Hofmann, B 14, 665)

Distinguished by the production of a crystalline tetrabromide, fusible [114 5°] and volatile with-Gives no pp with soluout decomposition tions of silver or copper, and probably has the constitution (CH₂), C C CH₂, or β-dimethyl-

allene

6 Isoprene (about 37°) Originally obtained (v Gr Williams, Tr 1860, 241), along with caoutchene and heveene, by destructive distillation of caoutchous (q v) Formed also in notable quantity by the action of very low red heat upon turpentine oil and its isomerides (Tilden, C J 45, 410) A colourless, lumpid liquid, S G 6823 at 20°. Oxidises rapidly on exposure to air,

forming a syrupy compound which, on being quickly heated, often explodes Contact with strong acids in the cold converts it into a substance apparently identical with caoutchouc Combines violently with bromine, forming a tetrabromide which remains liquid at -20° and is decomposed by distillation. Absorbs hydro chloric acid, forming a mixture of mono- and di hydrochlorides C.H. 2HCl (145°-150°), un-Oxidised by chromic acid to stable liquid carbonic, formic, and acetic acids, by nitric acid to oxalic and a small quantity of undetermined acid

Heated to 280° isoprene is converted into dipentene Ci, Hie, identical with the product from turpentine (v Terrenzs) (Bouchardat, C R 87, 654 a 89, pp 361, 1117) W A T PENTINENE CARBOXYLIC ACID v Hexi-

NOTE ACTO

Pentinene tricarboxylic acid C.H.O. s.c. C,H, C(CO,H),CH, CO,H

Allyl ethane tricarboxylic acid Got from its ether, which is made from sodium ethane tricarboxylic ether and allyl bromide (Hjelt, B 16, 333) At 160° it splits up into

Liput, B 10, 555) At 180° it splits up into allyl succinic acid and CO₂.

Ethyl ether Et₄A"' (c 282°)

FENTINOIO ACID C₃H₄O₂ [206°] A product of the oxidation of oil of turpentine by HNO₂ (Roser, B 15, 298) Tables (from water), all sol water

PENTINYL ETHYL OXIDE C,H₁₂O, t.e H, O C,H₁ (125°-130°) Formed from C.H., O.C.H., (125°-180°) Formed from C.H., Br OEt and alcoholic potash at 155° (Reboul, A 133, 86) Light oil Combines with bromine

PENTOIC ACID v VALERIC ACID

PENTONENE C.H. (425°) SG 808 VD 5 Occurs in oil deposited by compressed gas derived from bituminous shale (Etard a Lambert, C R 112, 945) Oil polymerises in the cold, becoming C10H12, which forms crystal

PENTONYL ETHYL OXIDE C,H,O s.c.
CH C CH, C(OEt) CH, (155°) V D 3 87 Got
by heating di chloro pentinene CH,(CCl CH,) with alcoholic potash (Combes, A Ch [6] 12, Colourless liquid, with unpleasant smell

PENTOSE Name given to compounds re sembling glucose but having only 5 atoms of carbon in the molecule, e.g tetra-oxy-valeric aldehyde

PÉNTYL Another name for the radicle Amyl

PENTYLENE v AMYLENE and PENTINENE PENTYLENE GLYCOL v DI-OXY-PENTANE PENTYLIC ACID is VALERIC ACID PENTYLIDENE v AMYLIDENE

PENTYLIDENE ACETONAMINE v ACRTON-

AMINE PEPPER OIL SG 15 875 The oil of black pepper is laworotatory ($\alpha = -32^{\circ}$) and contains a terpene (165°) which is laworotatory (a = -7 8°) and gives a crystalline tetrabromide (Eberhardt, Ar Ph [8] 25, 515, cf Dumas, A. 15, 159, Souberran, A 84, 327)

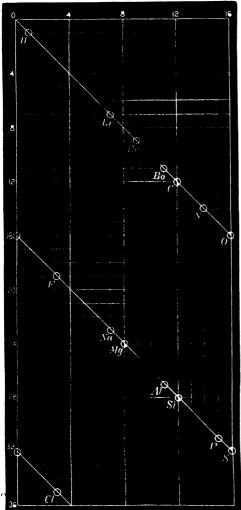
PEPPERMINT OIL The essential oil from

Mentha piperita contains menthol, CiaH.O, and a liquid terpene. The oil obtained by distilling M grvensus deposits crystals of menthol, and ap pears also to contain C,H,O, an inactive product of oxidation of menthol (Moriya, C J 39, 82) The oil from M viridis contains a tempere and C.H.O [225°] (Gladstone, C J 17, 1)

C., H., O [225°] (Gladstone, C J 17, 1)

PEPSIN The digestive ferment of the stomach (Schwann, Brucke, St. W 43, 601, Schmidt, A 61, 311) It also occurs sometimes in the urine (Stadelmann, Zert Biol 25, 208)

Preparation —1 The glandular layer of the stomach is extracted with dilute phosphoric acid,



the acid ppd by lime water, and the pp dissolved in dilute HClAq , the solution is then dialysed (Maly, J pr [2] 11, 104) -2 The mucous membrane of pigs' stomachs is macerated with water containing HClAq and the pepsin separated from the filtrate by adding NaCl (Scheffer, Ph [8] 2, 761, 783, 843) -3 The mucous membranes are kept 24 hours after death, and then extracted with glycerin The extract is ppd.

with alcohol (Wittich, J 1870, 894, Podwyssozky, Pf 39, 62)

Properties —Amorphous Does not give the xanthoproteic reaction, and is not coloured by H₂SO₄ and sugar It renders insoluble proteics soluble, converting them into peptones, this action is greatly enhanced by the presence of 05 pc HCl Digestion is more rapid at 37° than at 24° Dry pepsin does not lose its power

by heating to 100° (Huppe, C J 44, 101) According to Gautier (C R 94, 1192), pepsin contains some insoluble amorphous granules which also possess digestive power in presence of HClAq (cf Béchamp, Ol R 94, 970)

PEPTONES v PROTEIDS

PER Use of this prefix applied to inorganic compounds, for per compounds and per salts v the element the per compound of which is sought for, or the salts to the name of which per is prefixed. Thus peroxides are dealt with under Oxides, peroxide of nitrogen under Nitrogen, oxides of, perchloric acid under Chlorine, oxyacids of, permanganates under Manganese, oxyacids of

PEREIRINE C₁₉H₂₄N₂O [124°] An alkaloid, occurring with geissospermine in the bark of Pao Pereiro (Geissospermine Vellosis, Peckolt) It is separated from geissospermine by ether (Hesse, A 202 147) Amorphous powder, nearly insolwater, v sol alcohol and ethef Conc H₂SO₄ gives a violet red and HNO₂ a purple red colour — B'₂H₂PtCl₂4aq yellowish amorphous pp

PERIODÎĈ LAW In the history of modern chemistry we find several attempts to trace connections between the properties of the elements and their atomic weights Doberemer (G A 26, 331) was the first to show that a simple relation exists be tween the atomic weights of closely re Ca, Sr, and Ba are very lated elements closely related elements, and the atomic weight of Sr is the mean of those of Ca and Ba Again, Se has an atomic weight equal to the mean of the atomic weights of the closely related elements S and Te This doctrine of triad groups was further extended by Dumas (J 1851 291), Kremers (P 85, 56), and Lenssen (A 103, 121) Lenssen endeavoured to embrace all the elements in a classificatory system composed of 20 triads Pettenkofer (A 105, 188) pointed out that the atomic weights of analogous elements, eg the alkalı metals, form simple arithmetical series, and he emphasised the analogy between such na tural families of the elements and the homologous series of organic compounds

Kremers (P 83, 56), Gladstone (P M [4] 5, 313), Cooke (Am S (2) 17, 387), and Dumas (C R 45, 709) followed with generalisations differing only in detail from that of Pettenkofer

These discoveries did not, howe; er, herald any immediate great advance. It was, of course, interesting to find that elements showing gradational similarity of properties possess atomic weights, which are also, so to speak, numerically similar, but the newly discovered relationships

did not result in immediate practical applications, and did little more than emphasise pre-existing natural classifications The investigations altogether failed to afford a generalisation capable of embracing the groups of related elements in a complete classificatory system Instead of furnishing one inclusive scheme dealing with all the elements, they rather favoured a classification consisting of a number of isolated and partial systems, each system comprising only very closely allied elements, a classification similar in its imperfections to that which would have resulted in organic chemistry had chemists been content to differentiate empirically alcohols, aldehydes, and acids, without any knowledge of the relationships existing

oblivion from which it has but lately been withdrawn to the light of day (v N Dec 26, 1889; C N 63, 51)

Newlands was the first to look beyond the relations of analogous bodies merely, and to insist on a relationship of a higher order, connecting the properties and atomic weights of all the elements taken collectively

This relationship, first roughly indicated by Newlands in 1864 (C N 10, 94), was further developed in 1865 under the title of the law of octaves as follows -

'If the elements are arranged in order of their equivalents, with a few slight transpositions, as in the accompanying table, it will be observed that elements belonging to the same group usually appear on the same horizontal line

H Li Be B O N	1 F 2 Na 3 Mg 4 Al 5 Si 6 P 7 S	8 Cl 9 K 10 Ca 11 Cr 12 Ti 13 Mn 14 Fe	15 Co and Ni Cu 17 Zn 19 Y 18 In 20 As 21 Se	22 Br 23 Rb 25 Sr 24 Ce and La 26 Zr 27 Di and Mo 28 Rh and RJ		I 42 Cs 44 Ba and V 45 Ta 46 W 47 Nb 48 Au 49	Pt and Ir 50 T1 53 Pb 54 Th 56 Hg 52 B1 55 Os 51
------------------------------	---------------------------------------------------	------------------------------------------------------------------------	----------------------------------------------------------------------------	----------------------------------------------------------------------------------	--	-----------------------------------------------------------------	----------------------------------------------------------------------------

between these distinct, but closely connected, classes of bodies

The idea of arranging all the elements in the order of their atomic weights with a view to a more comprehensive classification based on the relations of these magnitudes and the salient properties of the elements, both chemical and physical, seems first to have suggested itself to M A E Deguyer de Chancourtois in the year 1862 His method of exhibiting the relationship was a geometrical one On a right cylinder with circular base he traced his 'telluric helix' at a constant angle of 45° to the axis On this curve lengths corresponding to the 'characteristic numbers' (atomic weights) were measured in terms of a unit equal to one sixteenth of the turn of the helix The extremities of these lengths were the 'characteristic points' for the elements De Chancourtois enunciated the principle that the relations between the properties of different bodies are manifested by simple geometrical relations between the positions of their characteristic points For instance, elements with analogous properties fall together on vertical This relation lines parallel to the generatrix becomes apparent when the cylinder is plane de veloped as in fig on p 808 It follows from this that the atomic weights of any natural group of elements are expressible in terms of the general algebraic formula (n+16m), where m is an integer, in other words, that the differences between the atomic weights of allied bodies are, in general, multiples of 16

16, 16+16=82, $16+(4\times16)=80$, $16+(7\times16)=128$ Other similar relations were developed by means of secondary helices

De Chancourtois, evidently absorbed in the numerical relations exhibited by members of the individual groups, omitted to consider sufficiently the relations of the various groups, and so he failed to give clear expression to the periodicity of properties which his telluric helix implies A mathematician and geologist, de Chancourtois
expressed himself in terms not at all calculated
to attract the attention of the chemical world
at large, consequently his work fell into an

It will also be seen that the numbers of analogous elements generally differ by 7 or some multiple of 7, in other words, members of the same group stand to each other in the same relation as extremities of one or more octaves in music $(C\ N\ 12,83)$

As will be seen. Newlands' law was retrospective rather than prophetic, 1 it recapitulated and coordinated old facts, but did not suggest new ones Though Newlands admitted the probability of the discovery of new elements, his rigid disposition into 8 octaves of the 62 elements then known neither admitted of interpolations nor suggested additions In his development of the conception of chemical octaves there was a too evident subordination of fact, and chemists gave but little heed to a classificatory scheme which formed octaves at the cost of grouping together elements chemically dissimilar, and then only succeeded in producing octaves varying in range from 8 to 10 constituent elements

In March 1869 Mendeléeff read a paper on the periodic law before the Russian Chemical This periodic law was nothing else than a generalised and developed form of the law of octaves, the conceptions underlying both laws being practically identical Yet Mendeléeff's law was the law of octaves so elaborated and expanded that it at once attracted general attention Operative not only in the realm of the known, but boldly presuming to deal with the unknown, this periodic law clearly indicates methods of testing its own validity states that the properties of the elements, as well as those of their compounds, are periodic func-tions of the atomic weights of the elements. That is to say, if in a co-ordinate system atomic weights be measured along one axis, and any measurable property along the other, a line joining the loci of the intersections of corresponding abscissæ and ordinates will form a sinuous curve showing maxima and minima. As the atomic weight increases the property considered will not increase or diminish indefinitely, but will exhibit periodical waxing and waning in intensity.

Contemporaneously with the enunciation of | the periodic law by Mendeléeff, but quite inde-pendently, L. Meyer (A Suppl 7, 854) showed that such a periodic curve results when the relatively measurable property considered is stomic volume (at wt +8 G in solid state). In fact, nearly every measurable property-physical and chemico physical—has been investigated, and in every case the law has been substantiated.1 On examination of the characteristic ultra-violet spectra of the elements, Hartley $(C \ J \ 41, 84)$ found these to vary periodically in such a way that elements belonging to the same group have analogously disposed spectra, in fact, Hartley made use of this generalisation in assigning Be (vide infra) a place in the periodic system ($O\ J\ 48,\ 316$, see also Lecocq de Boisbaudran, $C\ N\ 1886\ (2)\ 4$) Laurie ($P\ M\ [5]\ 15$, 42) obtained periodic curves when he plotted out the values of the heats of formation of haloid compounds of the elements in diagrams in which atomic weight was taken as the other variable In this connection also Carnelley investigated the melting-points, boiling points, and heats of formation, of the halogen compounds of the elements $(P \ M \ [5] \ 8, 1)$, the colours of corresponding compounds of the elements $(P \ M \ [5]$ 18, 130), the occurrence of the elements in nature $(P \ M \ [5] \ 18, 194)$, the salient physical properties of the compounds of the elements with alkyl radicles (P M [5] 20, 259), and finally the magnetic properties of the elements $(B\ 12,\ 1958)$ Carnelley and Walker have examined the relation of the phenomenon of the complete dehydration of hydrated oxides to the periodic law (C J 53, 59) Prud'homme (C R 112, 236) found that the shades produced by using different metallic oxides to fix one and the same colouring matter varied periodically with the atomic weights of the metals Brauner and Watts found confirmation of the law in studying the molecular volumes of the oxides (B 14, 48) Roberts Austen experimented with a like result on the tenacity of gold when alloyed with about 2 per cent of other metals (Pr 43, 425) Recently, Sutherland (P M [5] 30, 318) has asserted a periodicity of the vibration-periods of the atoms of elements at their melting-points

For a fairly complete summary of such investigations showing that the atomic weights of the elements are the true variables which determine the properties of matter v Meyer's Modern

Theories of Chemistry, pp 119-154

At first sight it might seem that the best method of giving detailed expression to this periodic law would be the geometrical one of tracing periodic curves as above indicated, but in the present state of science this is impossible, for we have yet to learn methods of measuring chemical properties. Further, the periodicity which Mendeléeff asserts is peculiar in its discontinuity, and contrasts strongly with the continuous periodic curves of the geometer, such, for instance, as the curve of sines. Conclusions respecting any point on such a curve as the curve of sines, where the periodicity may be called continuous, are warranted, but unless geometrical analysis be modified in a special manner

the connecting by a continuous curve of the loci of intersection of ordinates and abscisse in a coordinate system, of which properties and atomic weights are the variables, amounts to a virtual negation of the indivisibility of atom, and to an assertion that the number of elements is infinite No elements intermediate betweer, e.g., silver and cadmium, and with atomic weights between 107 6 and 112, are known Even if they existed, we could not for a moment suppose that they would form oxides with formulæ containing a fractional number of oxygen atoms Yet, as will be seen later on, if the periodic law were represented and interpreted geometrically it would certainly involve not only the existence of such intermediate elements, but also the existence of oxides and other compounds incompatible with the fundamental conception of modern chemistry -the conception of the atom

For these and similar reasons it is not only desirable but imperative that the periodic law should have a non geometrical representation at present. Let the elements (hydrogen excepted) be arranged in order of their atomic weights. It will then be found that the properties vary gradually as the value of the atomic weight in creases, that when the eighth element is reached we have reproduced in varying intensity many of the properties characterising the first. The same is true of the fifteenth element. Similarly, in the ninth and sixteenth elements we have the recurrence of the propert es of the second in the series, and so on

If now, instead of this linear disposition, we arrange the elements in two dimensions, placing elements with analogous properties in the same vertical lines, and if we suppose that certain elements exist which have not yet been isolated, we obtain the table on the following page (taken from Brauner ($C\ J$ 41, 68), and differing in slight details from the one first proposed by Mendeléeff), consisting of twelve horizontal rows and eight vertical columns

The horizontal rows are called 'series,' and consist of elements whose properties vary gradually from one member to the next. It will be seen that hydrogen, on account of the anoma lous relations between the value of its atomic weight and those of succeeding elements, is regarded as constituting a series in itself. The vertical columns are called 'groups,' and comprise elements with similar properties, i.e. elements which would occur at comparable points on periodic curves, could such be traced as already indicated. The similarity in properties shown by members of a group is a regularly gradationed one, and while in a series the properties of the elements vary in kind, in a group the variation is, speaking widely, one of degree only

It will be noticed that the perfect symmetry of the table and the analogy which for the first few series it shows with the notes of the dia tonic scale disappear when the end of the fourth series is reached. The three elements Fe, Ni, and Co, following upon Mn, and showing no analogies with the elements of Gropps L., IL, and III respectively (where, guided solely by considerations of symmetry, we should be inclined to locate them), inaugurate the eighth group of Mendeléeff's table, a group containing many of the more important industrial metals, all veri

¹ It should be noted, however, that the specific heats of the elements in the solid state do net vary periodically with the atomic weights.

	GROUPS									
2	I.	II.	III.	IĀ	▼	Ar	VII.	VIII.		
_	R,	R,O,	R,O,	R,O.	R,O,	R,O.	R.O.	R ₂ O _e		
1 2	H=1 Li=76	 Be=9			N=14	— 0=16	F=19			
3	Na=23 K=39	Mg=24 Ca=40	Al=27 So=44	Si=26 Ti=48	P=31 V=51	S=32 Or=52	Cl=35 5 Mn=55	Fe=56 Ni=586 Co=59 (Cu=63)		
6	Cu=63 Rb ●85	Zn=65 Sr=87	Ga=70 Y=89	Ge=72 Zr=90	As=75 Nb=94	Se=79 Mo=96	Br=80 ? 100	Ru=101 Rh=103 Pd=106 (Ag=108)		
7 8	Ag=108 Cs=133	Cd=112 Ba=137	In=114 Ia=139	Sn=118 Ce=140	Sb=120 Di=143	Te=125 ? 149	I=127 Sm=150?	? 152—156 4 Elements ?		
9	4 Pla	ments 156 to	100.0		Er=166	? 167	? 169			
10	? 170	? 172	Yb=178	? 178	Ta=182	W=184	? 190	Os=190 Ir=192 5 Pt=194 (Au=197)		
11	Au=197	Hg=200	Tl=304	Pb=207	Bi=208	2 9 Element	219 to 290 2			
12	₹ 8 E	ements 220 t	0 230 ?	Th=232	? 287	? 2 Elements 212 to 220? U=240 ? 245				

(In this Table the atomic weights are only approximate.)

closely allied from a chemical point of view (A Suppl 8, 147), and a group anomalous in that even series only are represented, three elements occurring in each series According to Mendeléeff, the metals Cu, Ag, and Au, similar in many respects to the elements of Group I, nevertheless show, in their higher oxidation forms and physical properties, such analogies with the members of Group VIII as to warrant their double representation in the table (A lc p 152) It should also be noticed that the table is so constructed as to indicate a subdivision of each of the groups I -VII into two sub groups or 'families,' one family in each case being constituted of members of even series only, the other of members of odd series only This subdivision is more apparent in the following tabular ar

the hydroxyl derivatives of the paraffins into the minor classes of primary, secondary, and tertiary alcohols—is that, although there is a general similarity between all the members of a group, yet there is a more pronounced similarity be tween the members of odd series and the members of even series respectively, in other words, alternate members of a group are in general more closely related than successive members

Nevertheless the advisability of a rigid subdivision of all the groups as indicated is open to question. In the case of Group II this division is undoubtedly warranted. Mg, Ca, Zn, Sr, Cd, Ba, Hg have all certain properties in common But the family Mg, Zn, Cd, Hg, on the one hand, and the family Mg, Zn, Cd, Hg, on the other, have respectively so many similarities that we are

				Series			
Bub-groups	1	2	4	6	8	10	12
Ia.	}	Li= 7-02	K = 89 11	Rb= 85 5	Cs=1329		
Ha	ł	Be= 9	Ca=40	8r= 87·6	Ba = 137		-
IIIa.	1	B=11	Sc=44	Yt= 89 1	La=1382	Yb=178	
IVa	i	C=12	Ti=48	Zr= 90 6	Ce=140.2	-	Th=2326
Va.	l	N=1403	V=514	Nb= 91	D1 = 142 3	Ta=1826	
VIa.	l	O=16	Or=521	Mo= 96	_	W=184	U=2396
VIIa.	l	F=19	Mn=55	_	_		
VIII.	l .	1		Ru=101-6 Rh=1035		Os=190 8 Ir=193 1	
	I	1	Co=59 Cu=684	Pd=1066 Ag=107 92		Pt=195 Au=1973	
Ib	H=1.007	Na=23-05	Ou=63 4	Ag=107 92		Au=1973	
Пb	1	Mg=24 8	Zn=65 3	Cd=112		Hg = 200	_
IIIb.	Í	Al=27	Ga=69	In=1137		T1=204 18	_
I¥b.●	ì	St=284	Ge=728	Sn=119	_	Pb=206 95	_
Vδ	ł	P=81	As=75	Sb=120	Er=1663	Bi = 208-9	_
VIb.	ł	8=3206		Te=125	-	-	-
VIIb,	1	Cl=35 5	Br=79.95	I=126 85	_	=	1 =
	1	8	5	7	9	11	13
	SERIES						

(In this Table O=16 is the starting point of atomic weights. See F W Clarke, C N 63, 76)

rangement 30f the elements which Mendelseff suggests as a truer representation than the foregoing table of the peculiarly compounded periodicity which obtains

city which obtains

The reason for this subdivision—which may
act inaptly be compared with the subdivision of

rangement 30f the elements which Mendeléeff | justified in making the subdivision in this case

(v Classification, vol 11 p 204)
But in the case of Group V, the 'family characteristics' do-not so predominate over those of the group, N, P, V, As, Sb, &c, are all so much slike in properties that here a resolution

into families is by some regarded as superfluous, this group, it is said, is more conveniently studied as a whole, for now the group characteristics' predominate over those of the families

(v vol n p 210)
The elements constituting the eighth group have so many characteristic properties in common that subdivision of the group in any way

would be artificial and unnecessary

There have been various other methods (diand tri-dimensional) suggested for representing the periodicity in properties of the elements, but none of them perhaps sums up the facts known more simply and clearly than Mendeléeff's table (v Meyer's Modern Theories, p 120, Reynolds, N 34, 423, Crookes, C J 53, 503, Bayley, P M [5] 13, 26, Kremers, Physikalisch-chemische Untersuchungen, Wiesbaden, 1869-70, Baumhauer, Die Besiehungen swischen den Atomgewichte und der Natur der Elemente, Braunschweig, 1879)

On inspecting his table in the light of known facts, Mendeléeff was led to make the following generalisations .-

(1) Excluding Series 2, the most markedly non-metallic elements occur in odd series 1

in the formation of diglycollic acid by the interaction of LiOH and monochloracetic acid N 18 more closely related to P than to V; O to S than Again F and Mn contrast very strongly On this account Mendeléeff has styled the elements composing Series 1 and 2 Typical Elements Though the differences (averaging about forty) between the atomic weights of Na and Mg (Series 3) and those of the corresponding elements Cu and Zn (Series 5) are greater than those derived from a consideration of Series 2 and 4, yet the properties of Na and Cu on the one hand, and of Mg and Zn on the other, contrast so strongly, in Mendeléeff's opinion, as to induce him to enrol Na and Mg also among the typical elements open to question whether the differences between Mg and Zn are sufficient to justify the classifi cation of the former as a typical element, most chemists would probably find in Na the limit of the typical elements Meyer, however, insists that the differences between Mg, Al, Si, and the other members of the corresponding groups is such as to justify the enrolment of these three substances among the typical elements, as follows .-

bicarbonate, its difficultly soluble carbonate, and

(11) Omitting Series 2, only members of odd | series form compounds with organic radicles (the organo metallic compounds) 2 Just as the hydrides of Pd, Cu, and Nb contrast strongly the following as perhaps a more with the hydrides of elements belonging to odd sition of the typical elements -

Yet the typical elements after nitrogen exhibit so little analogy with the groups placed below them in the above scheme that Meyer proposes the following as perhaps a more scientific dispo-

series, so organic compounds of members of even series (should such be hereafter discovered) will possess properties very different from those of similar compounds with which we are at present acquainted

Mendeléeff expressly omits Series 2 in making these generalisations If, excluding the very in complete Series 10 and 12, we tabulate the differences between the atomic weights of corresponding elements of Series 2 and 4, 4 and 6, 6 and 8, we find that, whereas the mean difference of corresponding elements of consecutive series is about 42, the mean difference for Series 2 and 4 is only 34 5 Since properties and atomic weights are dependent, we should expect from the above relations that the properties of the elements of Series 2 would contrast with the general properties exhibited by the other members of the families which they head Such is actually the case to a greater or less extent with all the members of Series 2; eg Li differs from the other alkalı metals, and approaches the alkalıne earths in its insoluble phosphate, its easily soluble

Some go still further than Meyer, and regard H to Cl inclusive as typical elements, but such extreme views can scarcely be regarded otherwise than as unwarranted subordination of fact to considerations of symmetry suggested by Men deléeff's table

Mendeléeff compares his so called typical elements to the lower members of homologous series in organic chemistry, which, as is well known, possess many properties peculiar to themselves and unrepresented in the higher members In this connection contrast H2O and CH₁O with the higher alcohols of the $C_n H_{2n+2}O$

While some disapprove of the title 'typical elements,' maintaining that this nomenclature connotes exactly the opposite of what it should, seeing that the typical elements are by no means types (as this word is generally understood) of the groups or even of the families which they head, others attempt to justify Mendeléeff's The former would rechristen nomenclature the typical elements as anomalous elements, the latter would either find in the typical element of the group a combination of individual characteristics of each of the constituents of the sub-groups (vide vol. ii. p 207), or in the typical elements as a class a representation of the gamut of variations of chemical properties.

(iii.) The passage from even to odd series is

¹ To render these generalisations unconditional Walker (O N 63, 261) has proposed that H to P be regarded as constituting Beries 1, Series 2 being regarded as wanting If this proposal is adopted, it becomes hardly necessary to differentiate typical elements (v $iv_i ra$). Recently it has been shown by Winkler (B. 24, 873, 1966) that the same generalisation can scarcely be applied to the hydrides also.

accompanied by a more gradual change in the properties of the elements than is the passage from an odd to an even series. This fact is in a This fact is in a manner emphasised in Mendeléeff's second table

(iv.) As the at wt increases in each group -(a) The elements become more electropositive, and their oxides become more basic. This is well exemplified by the oxides of the types B_2O_3 and B_2O_3 formed by the elements of Gr ∇

(β) Corresponding compounds of the elements become more easily reduced. This is well instanced in the triplets S, Se, Te, and Cu,

 (γ) There is a tendency to form stable oxides (and the saits corresponding to these) containing less O than the maximum salt-forming oxide characteristic of the group (vide infra) Thus, the characteristic oxide of Gr V is of the type R₂O₃, and the haloid and oxyhaloid salts of the lower members of the group P, V, Nb, belong to this form, eg PF₃, VOCl₃, NbCl₃, but B₁, which is the highest known member of Gr V, forms salts corresponding to the oxide R₂O₃ Again in Gr IV no oxide of Si having the formula SiO is known, SnO is known but is unstable, while PbO figures as the stable oxide of

(v.) Periodicity of valency and limiting forms It has long been admitted that the atoms of those elements which form hydrides are limited with respect to the maximum number of H atoms which they can hold in combination, but it was only with the introduction of the periodic law that it was noticed that this limited power of combining with H atoms varies in a regularly periodic manner with the atomic weights Little is as yet known of metallic hydrides, so that we have to look to Groups IV -VII, consisting of what may broadly be called the non-metals, for a confirmation of this periodicity

For instance

Gr IV furnishes us with CH4, SiH4,

NH, PH, AsH, SbH, Gr V ,, Gr VI OH₂, SH₂, SeH₂, TeH₂, FH, ClH, BrH, and IH ,, Gr VII In the same way, but more perfectly, the law teaches us that the maximum number of oxygen atoms with which the elementary atoms can severally combine to form definite salt-forming oxides -either acidic or basic, as the case may be-also varies periodically with the atomic weights of the elements The oxides characteristic of Gr IV are of the type R2O4 (or RO2), those of Gr V of the type R2Os, and so on regularly till we come to the eighth group, which has maximum salt forming oxides of the type R₂O₆ (or RO4) In carrying back this regularity to the groups I -IV, consisting for the greater part of metals we find that it assigns to each of these groups exactly that type of oxide which we know to be characteristic of the individual members of the group Hence we are justified in broadly asserting that the types of the hydrides (so far as they are already known), as well as those of definite salt-forming oxides, are periodic functions of the atomic weights of the elements the present time they are merely considerations of a regular periodicity, and not facts actually known that lead us to assign R.O. to Group VII as its characteristic oxide Fluorine

so far as we know, forms no oxides at all; and

the highest halogen oxide is of the type R₂O₄. In fact, Mn is the only member of the group that has an oxide conforming to the type R2O, Yet, having regard to the successes (to be detailed later) attendant on other predictions of the law, founded only on considerations of symmetry and general plan, all this is simply tantamount to admitting that the conditions of the existence of such oxides as Cl2O2, I2O2, &c, are legitimate subjects for research Again, ın Gr VIII the only oxides of the form RO, yet isolated are RuO, and OsO,, but chemistry is by no means a completely worked out science wanting nothing, and the periodic law would be at fault did it fail to mirror forth such shortcomings and imperfections as still exist forms of complex oxyacids are determined by the forms of the maximum oxides, and may be derived from these by replacing O by its equivalent (OH)₂ or H₂ Thus from SO₃ we can derive the chief oxyscids of S SO₂(OH)₂, SO₂H(OH), and SO₂H₂.

The highest compounds of the elements with halogens also correspond in type to the maximum oxide forms, and therefore exhibit a regular eriodicity In many cases, however, e.g TeCl., ICl, AsCl, only haloids lower in type than the maximum oxides are known, but in no case is a simple haloid known of higher type than the maximum oxide of the element considered

Against the doctrine of a maximum oxide form peculiar to all the members of each group, and of the types assigned (Table, top p 811), the existence of such oxides as K_2O_3 , BaO_3 , &c, has been adduced In reply it has been pointed out that these oxides belong to the class of peroxides,2 all of which are distinguished by their instability in the presence of the so-called 'contact agents, as well as by their mability to form corresponding salts with a given basic or acidic oxide, as the case may be, and that a generalisation explicitly extending only to salt forming oxides, strictly so called, cannot be impugned by considerations originating in the study of a class of bodies lying wholly without the pale of its juris-

Yet this reply is scarcely satisfactory, for in certain cases we are bound, in order to justify the principle advanced, to recognise such bodies as PbO, and Bi₂O₃—oxides currently regarded as peroxides But PbO₂ is undoubtedly an acidic oxide, forming with basic oxides the corresponding plumbates, and Bi2O, would also seem to have the power of forming with strong basic oxides unstable bismuthates—so unstable, in fact, that their true composition is still very doubtful. Hence Mendeléeff (B 15, 242) asserts that the oxides in question are not peroxides, for, according to him, true peroxides such as BaO, Cr.O., TiO., H.O., cannot form corresponding salts, and must of necessity contain relatively

Some of the recently isolated carbonyl compounds of the elements of Group VIII. conform to type MO. (C J SF, 749., 59, 1090.) C R. 113, 1431)

"It seems more than probable that a wider study of the higher forms of oxidation will result not only in the discovery of several new peroxides, but also of a distinct periodicity of type amongst this class of bodies also.

"The recent isolation of persulphates, M'80. by Berthelot (C R. 113, 1431) and Marshall (C J s9, 771) does not harmonise with Mendeleest's views. Nor does not harmonise with Mendeleest's views. Nor does compounds of Me and W

more O than do the maximum salt-forming oxides (acidic or basio) as defined by the periodic law (v also Piccini, B 18, Ref 255). Still the case of CuO (which cannot be regarded as a peroxide) presents a difficulty, if Cu is rightly placed in Gr. I, for, in accordance with this position of Cu among the elements, the principle under discussion would lead us to expect a maximum salt-forming oxide of the formula Cu.O

Cu.O
In conclusion it may be said that although there undoubtedly is some connection between the at wts of the elements and the types of exides they form, yet with the imperfect methods which we have of representing the periodic law, and in the absence of any firmly grounded and generally recognised classification of exides, it is impossible to give a hard-and fast enunciation

of this connection

We may assert that, so far as we are aware, a single atom of an element combines with at most four atoms of O or four atoms of H. The periodic law teaches us that the hydrogen holding power of the non-metals decreases regularly with increasing at wit, while the oxygen-holding power, as measured by the group oxides, increases regularly in such a way that the sum of the number of equivalents of both is equal to eight. For instance, S combines with two equivalents of H to form H₂S, it cannot, therefore, form a higher salt forming oxide than SO₂, which contains six equivalents of O

Some chemists have proposed to extend this principle to the metals, i.e. to Groups I, II, and III Since Na combines with one equivalent of O to give a salt-forming oxide, it must, they argue, combine with not more than seven equivalents of H or its equivalent Similarly Ba combining with two equivalents of O must combine with six equivalents of H, and so on But Brauner (Sitz W, 'Math-naturwiss Classe,' 84, 1165) would go still further Let X denote a single equivalent of any element or radicle

$$(X = H, \frac{O}{2}, \frac{S}{2}, \frac{N}{3}, OH, &c)$$
, then he asserts

that the whole of the compounds of Na will be constituted on the types NaX or NaX,, or on types intermediate between these two, that all the compounds of Ba will be constituted on some of the types included in the scheme BaX2 BaX, and so on In short he would make out that there are certain limiting forms defining the complexities not only of the binary, but of all the compounds formed by each element, and that the range of these limits varies regularly and periodically with the atomic weights order to substantiate this view, recourse has been had to formulæ not yet authorised by Avogadro's law, and sweeping assumptions are made as to the dispositions of the constituent atoms or atomic groups in the molecules or reacting masses of the bodies taken to exemplify this doctrine of limiting forms Thus, out of all the numerous compounds of the alkalı metals, the only one that can be found conforming to the type RX, is the substance NaOH 3H2O, and then only provided we manipulate the constituent atoms as follows · Na(OH)(OH), H, Si belongs to Group IV, therefore, according to Brauner, all its compounds ought to be of the type RX. Its oxide SiO₂ certainly conforms to the rule, but the highly characteristic body SiH₂F₆ does not. Again, can such compounds of Pt as PtCl₂8H₂O, PtCl₂2HCl6H₂O, &c, be regarded as belonging to the type RX₂? These are one or two examples, out of very many, of the kinde of difficulties that stand in the way of a full recognition of Brauner's extension of Mendeléeff's views (v Classification, vol ii pp 210-13)

The idea that the valencies of the atoms vary regularly and periodically with their weights is one which has often been mooted, but in the absence of any recognised definition of valency

it is an idea difficult to criticise 🛰 :

If, as was originally done, the valency of an element be referred back to some constant objective attribute of the atom, and measured by the number of H atoms with which the given atom can combine, a partial periodicity involving only groups IV _VII is undoubtedly apparent

Group	14	V	ΔI	VII.
	CH, SiH,	NH. PH. AsH.	OH. SH. SeH.	FH ClH BrH
Valency	IA	111	II	I.

This conception of constant valency not only lacks in generality (since out of the 70 or so ele ments only some 17 combine with H), but for the establishment of its validity demands a division of compounds into the two classes of atomic and molecular—a division altogether too artificial to be admitted If we forgo the idea of constant valency, and merely attempt to define the valency of an element as a number expressing the maximum number of monovalent atoms (H, F, Cl, Br, I) with which a single atom of the element in question combines to form true gaseous molecules, i e if we give a mere name to the maximum number of 'equivalents' represented in an atom, the alleged periodicity is still far from being perfect, as the table on the follow ing page, embracing the latest results, shows

Regarding this question of valency in the light of what has been said of limiting hydride and oxide forms, it is at least apparent that our crude conceptions of valency do not admit of a satisfactory quantitative interpretation. The sulphur atom fixes 2 equivalents of H and 6 of O, the arsenic atom fixes 3 equivalents of H and 5 of O. Why, we may ask, should we decide to overlook these essential relations exhibited by the oxides, to say nothing of the peroxides, and regard the valencies as deduced from the hydrides and haloids merely as fundamental properties of the atoms?

Mendeléeff himself regards the theory of valency as extreme and not very valuable Originating in the study of carbon compounds, valency finds in the domain of organic chemistry its only legitimate application, for the carbon atom, in accordance with its position in the periodic scheme, combines with equal numbers of equivalents of H and O, and, further, carbon compounds do not form so-called molecular compounds. He maintains that the forms of chemical compounds (including here isomerism, and therefore structural formulæ) are fully explained, without the spurious aid of a statical

3	GROUPS .									
Per tes	l.	n.	111.	IA	V	VI.	VII.	VIII.		
1	Ηı									
3	ы	Beli	Bin	Ot+	Mm	On	F4			
3	Na	Mg	Alm .	Site	Pr	8n	Clı			
4	K ⁱ	Ca	Se	Tit	Δi4	Criti	Mnii	Fem Ni Co		
5	Cu	Znü	Gam	Ge⁴▼	Aşiii	Sen	Bri			
6	Rbi	Sr	Y	Zriv	Nb▼	Mo▼		Ru Rh Pd		
7	Agl	Cdu	Iniii	Sniv	Sb▼	Te⁴	Iı			
8	Cal	Ba	La	Ce	Di					
9					Er					
10			Yb		Tav	M41		Os Ir Pt		
11	Au	Hgu	Tli	Pbiv	Bi ^{tti}					
12		1		Thiv		Ui≠				

(The index numbers express valencies.)

theory of valency, in terms of the periodic principle together with more generalised views on substitution involving the recognition of Newton's third law, which states that action and react on are equal (v A Suppl 8, 211, N 40, 354)

Uses of the Perioduc Law —An induction of any value should be suggestive of deductions admitting in their turn of experimental confirmation. Judged from this standpoint, the periodic law is well worthy the exalted position accorded it among the principles of chemistry, for it has opened up immense fields of research which deduction has already, to a small extent, successfully explored.

In order to maintain a general identity of properties in the vertical columns or groups of Mendeléeff's table, it was found necessary to make gaps here and there, to leave certain series unrepresented in the various groups was asserted that these empty places in the scheme were the positions of undiscovered elements for which Mendeléeff proposed a provisional and temporary nomenclature Thus, in the year 1869, the element next to Ca = 40 with a higher atomic weight was Ti = 48, but Ti could not find a place in Group III Series 4, as its properties resemble those characterising Group IV and show no analogues with those of the other members of Group III Tiwas accordingly placed in Group IV Series 4, and the vacancy in Group III. Series 4 was assigned to a then unknown element provisionally styled ekaboron The principles of this nomenclature are very simple The predicted element takes its temporary name from the one immediately above it in the group family, the Sanskrit prefixes eka-, dvi-, tri-, &c. being prefixed according as the unknown element is one, two, &c , removes lower down in the family than the name determining element

Those elements of a family which stand immediately above and below a gap, together with those which immediately precede and succeed it in the series, are called the atom-analogues of

the element to which the gap corresponds Thus B, Yt, Ca, and T1 are the atom analogues of ekaboron Now it follows from the very nature of the law that the properties of any given element must be determinable from those of its atom analogues, that the properties of ekaboron, for instance, must be similar to, but intermediate in intensity between, those of B and Yt, and at the same time while dissimilar from those of Ca and Ti, they must show an intermediacy in their dissimilarity Hence it becomes possible to predict the properties of still undiscovered elements, the mean of means of the properties of the atomanalogues forming the basis of the prophecy How closely the properties of ekaboron thus predicted by Mendeleeff tallied with the properties of So experimentally investigated ten years later by Nilson is shown in the article Atomic and Mole-CULAR WEIGHTS (vol 1) Even were this case of ekaboron an isolated one, the wonderfully exact concordance between prediction on the one hand and experimental realisation on the other would go far to establish the periodic law as a generalisation of the highest order But ekaboron is not an isolated example of the prophetic infallibility of the law which has as strikingly asserted itself in connection with the two recently discovered elements Ga and Ge (q v vol 11 597, 610) The periodic law is and will be to the science of chemistry what Newton's law of gravitation was and is to the science of astronomy Neptune had its place assigned in the worlds around us before it was seen, before they were discovered Sc, Ga, and Ge had their properties detailed and their places assigned them among the elements, which by means of the periodic law have been raised from the level of 'mere fragmentary and incidental facts in nature

The validity of Mendeléeff's generalisation has also been confirmed in connection with the question of atomic weights Before the enun

It yet remains to be seen whether the new element, austriacum, separated by Branner from tellurium ores, will identify itself with dvi tellurium, whose properties have recently been specified by Mendeleeff.

ciation of the periodic law the values for the atomic weights formed a series of isolated and purely empirical numbers, the atomic weight of an element once ascertained, there was nothing in the actual numerical value itself, even when considered along with the properties, either to confirm or cast doubt on it as the true atomic weight But the periodic law teaches that the atomic weights are by no means disconnected quantities, but that, taken in connection with the properties of the elements, their values constitute a series of mutually corrective numbers; in short, the law gives significance to the expression 'the probability of an atomic weight'

In dealing with this aspect of the law it will be well to distinguish two sets of cases

a. Those in which the law has actually fixed certain atomic weights indeterminable at the time by other means

8 Those in which the law has merely served to correct the values of atomic weights inaccurately determined by the usual methods

As illustrative of a we may consider the case of Be 1 The equivalent of Be having by accurate experiment been fixed at 451, it follows that the atomic weight must be numerically equal to $n \times 4$ 51, where n is an integer At first chemists were led to assign the formula Be₂O₂ to the oxide of Be on account of its isomorphism and many points of similarity with Al₂O₂ This taken in conjunction with the analysis of the oxide makes n=8, and consequently fixes the atomic weight as 18 5 But Brauner repeatedly emphasised the view that the oxide of Be has the formula BeO. and that Be has therefore the atomic weight 9 The keynote of the many arguments advanced by Brauner in favour of his views was the incompatibility of the existence of an element with an atomic weight of 135, and having the properties of Be, with the system of the elements as

arranged and classified by the periodic law In this system he argued that, not only was there no room for an element at wt 135, but that the proved existence of such an element would be totally subversive of the law other hand, he pointed out that a vacancy existed in Series 2, Group II, for an element with an atomic weight equal to 9, and a careful exami nation of the relations of the members of Series 2 as a whole to those of other series, taken along with the known relations of beryllium to the magnesium group, absolutely demanded in his opinion the filling up of this vacancy with the element beryllium Brauner's views were fully confirmed by Nilson and Pettersson, who succeeded in taking the vapour density of beryllium chloride, the application of Avogadro's law to their results gave the atomic weight of Be equal to 9 and the formula of the oxide BeO

We are inclined to wonder that the question of the atomic weight of so rare and comparatively unimportant an element as Be has originated such a large amount of work and stimulated such lively discussion, unless we remember that a question of much greater import than the atomic weight of Be was at issue, the validity of the periodic law itself was at stake. And it is of interest to note that Mendeléeff regards the substantiation of Brauner's views on Be as a confir-

³ In what immediately follors the values given for stomic weights and equivalents are only approximate.

mation of his law of the same order as the discovery by Nilson of Sc, the ekaboron of prophecy In a similar way the suggestions thrown out by the periodic law anent the atomic weights of U, Ce, and In have all met with corroboration Up to the date of the periodic law, Peligot's value 120 (= three times the equivalent 40) vas received as the atomic weight of U, but Mendeleeff (Ic. 178) suggested six times the equivalent, or 240, as the correct atomic weight, thus conferring on U the distinction, which it is now universally admitted to hold, of being the element with the highest known atomic weight

In 1870 the recognised atomic weight of Ce was 92 (2×46) Mendeléeff $(l \ \tilde{c} \ 186)$, however, showed that no place existed in the system for an element with this atomic weight, and showing the properties of Ce, but that a suitable vacancy existed in Group IV Series 8, if Ce was regarded as having an atomic weight one and a half times Mendeléeff's proposal the then accepted value has been fully justified by later work on the cerite metals $(C \ J \ 41, 68)$

The equivalent of In is 37 8, and formerly its atomic weight was taken equal to twice this, or But Mendeléeff (l c 174) showed the necessity of trebling the equivalent, thus assigning the value 1134, which is now accepted, to the atomic weight of this metal Similarly Mendeléeff suggested, what has not yet been very satisfactorily settled, that the atomic weight of yttrium is three times its equivalent number, 29 87 (v EARTHS)

The investigations on tellurium are fairly illustrative of the cases summed under the head The adoption of the value 128 for the atomic weight of Te as determined by Berzelius would necessitate iodine (at w 1265) taking precedence of Te in Series 7 of the periodic scheme, iodine being thus separated from the rest of the halogens and falling into Group VI with such elements as S and Se, with which it shows no analogies, and Te falling into Group VII with such elements as Cl, Br, and Mn, with which it in turn shows no kinship This violation of the principle of identity of chemical behaviour in the groups suggested some grave error in the ac cepted atomic weight of Te, an error causing this element to succeed iodine in the series in stead of preceding it, as the general plan of the law requires The subject has recently been investigated by Brauner (C J 55, 382), who for a second time has vindicated the law in a most striking manner by showing that the ci-devant tellurium is probably not elemental, and that the atomic weight of unalloyed tellurium is con siderably lower than that of iodine, being equal to about 125

In much the same way the law has 'ed to the correction of the previously accepted atomic weights of osmium, platinum, and gold

Formerly the accepted atomic weights of Os, Ir, Pt, and Au were in accordance with the scheme

Os > Ir > Pt > Au

But from the analogies existing between Os, Ru, and Fe, and the disposition of the first two series represented in Group VIII Mendeléeff (A. Lo.) predicted alterations of the atomic weights in accordance with the scheme

Os < Ir < Pt < Au.

This prediction has been fully confirmed by recent researches, it has not, however, yet been found possible to verify and substantiate the results now accepted for the last three metals

by the application of Avogadro's law

As well be seen from the case of tellurium, the periodic law in its relation to atomic weight determinations is broadly suggestive rather than accurately definitive It may be that ere long the discovery of the exact character of the periodicity, which at present we comprehend only vaguely, will raise Mendeléeff's law to the rank of an instrument for the absolute evaluation of atomic weights

Mendeléeff has repeatedly emphasised the great advantage accruing to students and chemists generally from an adoption of the periodic classification as a working basis—the |

atomic weights of elements constituting some of the natural families, and the analogy between the relations so obtained and those found between the molecular weights of members of homologous series, led Dumas (C R 45, 46, 47) and Gladstone (P M [4] 5, 313) to suggest that the so called elements are not primary, but are composed of two or more simpler elements

Pelopidas (B 16, 1868) called attention to the fact that the residues of hydrocarbons and nitrogenous organic bodies can be arranged in a periodic system, exhibiting in the number of members constituting the period, as well as in the gradual passage in each period from basic to acidic characters, a close analogy to Mendeléeff's periodic arrangement of the elements lowing are examples of the periods arranged by Pelopidas .-

Ш IV C₆H₁₃ C,H, C.H. C,H, C,H, C₆H, C.H. C.H. NH,C NH.C NH.O NHC NHO NO or NH₃(CH₃)

advantage lying in the great mnemonic power of the law, which, introduced into the disheartening chaos of accumulated chemical fact, at once resolved the complexities of the apparent and rearranged them so as to exhibit the simplicities of the real With one mental effort we commit to memory a large mass of facts which previously demanded so many independent but severally no less taxing mental exertions No longer is phosphorus studied as an element apart from arsenic, but the general scheme of properties of the whole fifth group is learnt, and the facts about P, As, V, &c, are easily mastered by re membering their small individual deviations from this general scheme

The law is also useful in that it points out the directions which should be taken by future research on the as yet unknown compounds of It is well called 'the well known elements finger post of modern chemistry' Examples of its utility in this respect have been indicated when treating of the law in its relation to limiting forms and to atomic weight determinations 1 In fact, every generalisation made in connection with the law suggests new work, organo metallic compounds of In and Tl, and of the form MR, (where R = organic radicle) must be forthcoming (v supra, ii), a suboxide of Cd having the formula Cd O is looked for $(v : ii \gamma)$, while various new peroxides of Mo and W, also a true peroxide of lead (Pb₂O₄) are very probable realisations of the future (v v)

Theories having their origin in the Periodic Law —Although, according to Mendeléeff (CJ55, 684), the periodic law, solely founded as it is on the solid rock of well-ascertained chemical fact, in no way indicates the nature of the elements nor predicates the existence of a unique matter, yet many have made it a peg whereon to hang theories respecting either the compound nature of our elements or the existence of a primordial matter

The simple relations holding between the The existence of Ourstan' assimide M_pH was foreseen by Mandelen (B 33, 8464). Vog. III.

The monovalent radicles NH₂(CH₂) and O₂H₁₁ undoubtedly show many analogies with the alkali metals, and CN has always been compared with forms the acid SO₂(OH)₂, so the radicle C₂H₄ forms the acid C₄H₆O₂(OH), and so on Carnelley (C N Nos 1375 and 1378), from

a consideration of the fact that the salient physical properties of the normal halogen and alkyl compounds of hydrocarbon radicles exhibit relationships similar to those of corresponding compounds of the elements, develops the view that elements are analogous to the hydrocarbon radicles both in form and function supposition that C and H are true elements, he then attempts to draw up a scheme of compounds of two primary elements, A and B, corresponding to Mendeléeff's scheme of the alleged elements, the compounds possessing the same 'atomic weights' and showing the same periodicity as the accepted In this scheme the elements appear elements as bodies of the type $A_nB_{2n+(2-x)}$, where xis the group and n the homologous series to which the element belongs, A is a tetrad element identical with carbon, and B, 'probably the ethereal fluid of space,' is a monad element with atomic weight =-21. These views of Carnelley are as much in advance of the earlier ones of Dumas and Gladstone as is the periodic law in advance of their disconnected schemes of classification, but they cannot be regarded otherwise than as ingenious and bold speculations indi cating the directions in which investigations on the rationals of the periodic law, and on the nature of the elements, will probably be prosecuted before we arrive at anything approaching the truth, either concerning the law on the one hand or the elements on the other

The attempt to discover some kind of unity in the sea of apparent diversities by which we are surrounded, or, rather, the natural inclination to assume such a unity, is as old as philo-sophy itself Prout merely gave scientific defi-niteness to the News of the early Grecian philosophers when he suggested that the atomic

weights of all the elements were whole mul tiples of that of hydrogen, which he iden tified with the primary matter, and in later years many have in turn thought to find in the periodic law a warranty for resuscitating the principle underlying Prout's law, at the same time either shifting the primary matter lower down in the scale, so that hydrogen itself appears as a highly condensed form of matter, or not attempting in any way to particularise concern ing the primary matter

The application of recent developments in spectroscopy, combined with improved methods of fractionation, has resulted in the view that many of our so called rare elements at least are not strictly elemental (v METALS, RARI, and At first sight the large increase in ELEMENTS) the number of recognised elements which this recent work involves would seem to militate against the indications of the periodic law But Crookes (C J 53, 487) has attempted to show that the new views may be brought into complete harmony with the periodic law if we will but admit into chemistry the principle of evolu tion Granted that the different forms of matter have been cyclically evolved from a primitive formless fluid (protyle), and that the units of Mendeléeff's generalisation are rather 'elementary groups' than true elements, then the periodic law with its limited accommodation necessarily follows (v also Mills, infra)

Some attempts have recently been made to express the atomic weights of the elements by means of general algebraic formulæ must be allowed that we are more likely to arrive at clear views regarding the periodicity of the elements through methods founded on the theory of numbers than through methods of a purely geometrical nature, yet many of the researches so far undertaken in this direction do not even promise to help towards the final solution of the periodic law In a few cases expressions have been obtained which, as they involve con stants numerically equal to some of the impor tant constants occurring in the principles of chemistry, may on a more detailed study culminate in a clearer understanding of the nature of the elements and the rationals of the law Mills (P M [5] 18, 393, 21, 151) arranges all the elements according to their atomic weights, and then subdivides this arrangement into sixteen groups He then finds that all atomic weights are involved in the logarithmic expression 15 p-15 (9375)x, in which x is an integer and p is the group number of the element considered ¹ This expression arrived at empirically is, according to Mills, such as we should expect if we regard the elements as stable, but more or less incomplete, stages in the polymerisation of the primary matter as it cooled. It is also noteworthy that the above expression, in that it points to the existence of an upper limit to our existing system of atomic weights, confirms views originally expressed by Mendeléeff

Carnelley's attempt (P M [5] 29, 97) to give a general expression to the atomic weights of the elements is of more interest in that it is founded, not on a conveniently assumed and artificial

G J Stoney has also arrived at a logarithmic expression for the atomic weights (Q.J. Proc. 1888, 55).

periodicity, but on the natural periodicity as this finds expression in Mendel(eff's schemes

Carnelley's equation is $A = c \ (m + \sqrt{v})$, where A = approximate atomic weight, m = a memberof an arithmetical progression depending on the series to which the element belongs, = number of the group of which the element is a member, and c is a constant

Excluding the elements of the first three series (typical elements), the expression for the atomic weights of all the other elements may be thrown into the more convenient form

$$A = c (3 + a - 9 + \sqrt{v}),$$

where a is the number of the series to which the element belongs In his paper, Carnelley notes the following points of interest the mean value of c = 6.64 is nearly identical with the mean value of the atomic heats of the ele Assume that c in the above formula ments actually represents atomic heat, then it follows that the specific heats of the elements should be

given by the expression $\frac{1}{m+\sqrt{v}}$, and this is found actually to be the case It should be noted, however, that these coincidences may be purely accidental and meaningless, being simply the re-

sult of the particular units adopted D C
PERSEITE C,H₁₈O, [188°] S 5 at 18°
Mol w (by Raoult's method) 179 (calc 212) A body resembling mannite, occurring in the fruit and leaves of *Laurus persea* growing in the tropics (Muntz a Marcane, *C R* 99, 38, *A Ch* [6] 3, 279, Maquenne, *A Ch* [6] 16, 5, *C R* 106, 1235, 107, 583, 658, Dehérain, *C R* 108, 101, cf Avequin a Melsens, A Ch [2] 72, 109) Extracted by water at 60°, the extract treated with lead acetate, filtered, freed from lead by H.S. concentrated, and mixed with MeOH Formed by reduction of mannoheptose by sodium amalgam (E Fischer a Passmore, B 23, 2228) Small needles (from alcohol), sl sol cold, v sol hot water and alcohol Its solution becomes dextro rotatory when borax is added Does not reduce Fehling's solution or undergo alcoholic fermen-On oxidation by nitric acid it yields mannoheptose C,H₁₄O, and finally oxalic acid Boiling HI and P give C,H₁₂ (c 104°) and C,H₁₅I (190°-200°) HCl yields C,H₁₄ (92°) An al coholic solution treated with HCl and benzoic aldehyde yields C,H12(CHPh)2O, [c 219°]

Acetyl derivative C,H,(OAc), Crystalline powder, insol water, sol alcohol Butyryl

derivative C,H,(O C,H,O), (o 300° in vacuo)

Netrate C,H₀(NO₂), [138°] Made from persente (1 pt), tuming HNO₃ (5 pts), and cone H₂SO₄ White needles, insol water, sol hot alcohol Explodes when struck
PETROCENE The highest boiling portion

of American petroleum contains, according to Hemilian (B 9, 1604), a hydrocarbon C, H₂₂ [above 300°] crystallising from benzene in yellow amine Prunier (A Ch [5] 17, 28) found carbopetrocene C₂H₂ [268°] which yielded C₂H₂C₃H₃N₃O, [185°] and C₂H₃C₃H₄N₃O, [135°] Prunier also found, in petroleum, petrocin C₁H₂? [102°] yielding C₁₂H₂O, H₃N₃O, [98°] and C₄H₂? [102°] yielding C₁₂H₃O, H₃N₃O, [98°] and C₄H₃? [102°] yielding C₁₂H₃O, H₃N₃O, [98°] and C₄H₃? [102°] yielding C₁₂H₃O, H₃N₃O, [98°] and C₄H₃? [103°] yielding C₁₃H₃O, H₃O, [98°] and C₄H₃O, a hydrocarbon C,H,? [119°] V also Petrolet M PETROLEUM. Earth oil, Rock oil, Naphtha,

Meneral oil, Erdöl, Sternöl, Petrole, Hurle de

pierre, Bitume haude Petroleum is the general name given to the natural oily liquids occurring in the earth at different depths and in many localities The natural oil is a mixture of several hydrocarbons, has a strong bituminous smell, but differ very considerably in its physical properties and chemical composition in large quantities in the United States, in the Caucasus, and in the country situated at the mouth of the Danube, in considerable quantities in Burmah and in Galicia, and has been found in Persia, the West Indian islands, Italy, parts of Germany, Switzerland, China, India, France, and England Its specific gravity ranges from 77 to 11, and its colour from pale yellow to brown, dark green, and black. The colour of crude petroleum not only varies with the locality, but varies from time to time in the same district B Redwood has recorded the colours of various kinds of crude petroleum (Journ Soc Arts, 34, 823, 878), and Lovibond's tintometer is used for determining the colour of commercial samples Crude petroleum varies considerably in its com position, that from North America consisting chiefly of hydrocarbons of the CnH2n+2 series, while that from Baku (Caucasus) contains in addition the hydrogenised aromatic hydrocarbons of the general formula C,H, (Beilstein a. Kurbatow, B 13, 1818, 2028) and small quantities of other hydrocarbons (Markownikow a Ogiobine, J R 15, 237, 307) Galician petroleum contains hydrocarbons of the series C_nH_{2n+2} and C_nH_{pn-q} (Freunc, A 115, 19), and also the hydrogenised aromatic hydrocarbons of the formula C_nH_{2n} (Lachowicz, A 220, 168) Crude petroleum also contains small quantities of compounds containing sulphur, nitrogen, and oxygen 028 per cent of nitrogen has been found in petroleum from Ohio, and 111 per cent in that obtained from California Beilby has also found 05 per cent of nitrogen in Baku oil and 0 188 per cent in Galician ozokerite Crude American petroleum contains at least 0 008 per cent of nitrogen (S C I 10, 120) Sulphur amounts to 187 per cent in certain Russian petroleums, and is present in that obtained from California Lima, Ohio, and Canada, but is absent from Pennsylvanian and West Virginian oils (Vohl, D P J 216, 47, Woodman, A C J [1891] 13, 179) From the variable composition of crude petroleum it follows that its volatility will be very different, the several consti tuents of crude petroleum extending from the gaseous members of the marsh gas series to solids which boil at 400° As a rule, the petroleum with lowest specific gravity is the most volatile and inflammable Crude petroleum also may contain water and sediment, and is tested commercially for its specific gravity, odour, colour, its feel when rubbed between the fingers, and the percentage of naphtha (or portion volatile below 150°) yielded on fractional distillation (Allen, 'Commercial Organic Analysis,' 11, 869, Nawratie, D P J 246, 828, 428) The flashing-point and burning point of petroleum are also important factors for ascertaining its commercial value, but these tests are usually applied only to the refined petroleum or kerosene. which consists of the more volatile portions of the crude oil which can be burned with a wick (Petroleum Act, 1871, 84 and 85 Vist. cap.

105, Petroleum Amendment Act, 1879, and for variation of flashing point with climate S C I. 1, 471, C N 40, 305, 49, 196) For calorific values of petroleum, see Deville, C R 72, 195, and 68, 348 Co efficient of absorption of oxygen is higher for petroleum than for water (Zeit Phys Chem 1, 70) When crude petroleum When crude petroleum is distilled, the various fractions are separately collected and used for a variety of commercial purposes. In America the distillation is conducted in large stills, and the first fractions, known as 'cymogene' and 'rhigolene,' are condensed by artificial cold and pressure fraction which next comes over, having a density increasing from 636 to 725 or 750, is separately collected, and when re-distilled is termed 'gasoline,' 'naphtha,' and 'benzine' The next fraction consists of oils of SG 75 to 84, and is known as 'kerosene' or 'photogene', while the residue is distilled in other retorts for lubricating oils, S.G. 84-9, and solid paraffin, until coke is left as a residue combustible with difficulty Petroleum ether is the fraction containing hydrocarbons of SG 625-665, and consists of 'rhigolene' and 'gasolene,' while petroleum spirit or benzoline consists of the 'naphtha' and 'benzine' fractions, SG 68-745

In Russia the petroleum is distilled in a series of stills in a continuous process, and yields three fractions light benzine, S G 754, 'gasolene' or heavy benzine, S G 787, and kerosene, S G 825 The residue on further distillation yields (1) lubricating oils, (2) solar oil, and (3) 'astatki,' which last is either used as fuel or distilled at a red heat, yielding benzenes and anthracene Baku petroleum contains only traces of solid hydrocarbons, while that from the Caucasus yields about 6 per cent of paraffin (B Redwood, S C I 4, 74)

In Germany the crude naphtha is refined into four distinct products

Petroleum ether (40°-70°) S G 0 640-0 650 Benzine (70°-120°) S G 0 700

Ligroin (120°-135°) S G 0 730

Cleaning oil (130°-160°) 8 G 0 745-0 750 (Schenkel, *Chem Ind* 13, 512)

Further details on the petroleum industry, and the properties and uses of these commercial products, will be found in Thorpe's DICTIONARY OF APPLIED CHEMISTRY

Early Leterature — Before 1864 very little accurate knowledge of the chemical constitution of the various petroleum oils was known, the earlier investigations chiefly recording the localities in which the oil had been found, its physical properties, and its behaviour on distillation

On the next page is a list of the more important of these examinations

AMERICAN PETEOLEUM Pelouze a Cahours (C R 54, 124, 56, 505, 57, 62) made a systematic investigation of the Pennsylvanian oil in 1864, and showed that it contained hydrocarbons of the formula C_nH_{m+p}, including representatives of every member of the series from C_sH₁₂ to C_{1p}H_{2p}. Ronalds added C_sH₁, C_sH_{2p}, and nO_sH₁₂ to this list (C J 18, 529) Above 280°, the boiling-point of the highest of these hydrocarbons, the oil yield 1 taible paraffins [45°-65°], and they when distilled in closed vessels were resolved into other C_nH_{2p+1} and C_nH_{2p} hydro-

Date	Description	Author	Reference	
1788	Black Hungary	Wintere	Crell's Chem Annal 1,498	
1791	Galicia	Martinovich	,, ,, 1,72	
1817	Naphtha of Miano, Parma	Saussure	Bibl Univ 1832, 160	
1829	Persia	Unverdorben	8 57, 2, 3	
1831	Rangoon	Christison a Gregory	T E 13, 118, 124	
1833	Persia	Blanchet a Sell	A 6, 309	
1836	Bavaria	Kobell	J pr 8, 805	
	Galicia	Torosiwiecz	R P 55, 15, 61, 398	
	Baku	Hess	P 84, 417	
1840	Miano	Pelletier a Walter	J Ph 26, 549	
1848 } 1849 }	Derbyshire	Ure a Mansfield	O J. 1, 249 Ph 7, 485	
1857	Rangoon	De la Rue a Müller	Pr 8, 221	
1858	Hanover	Eisenstück	A 118, 151	
-	"	Uelsm an	A 114, 279	
	Galicia	Freund a. Pebal	A. 115, 19	

earbons Schorlemmer found small quantities of benzene and its homologues, and Belistein a Kurbatoff a hydrogenised aromatic hydrocarbon of the C_nH_{2n} series, which they isolated and determined to be hexahydro metaxylene

The paraffin hydrocarbons above alluded to have also been examined in detail, and in many

cases their constitution determined

In the neighbourhood of the North American oil wells methane is evolved, and is associated with ethane in the gases which issue from the De la Mater well at Pittsburg (Sadtler, Am Ch 1876, 98, Fouqué, C R 67, 1015) Ethane, propane, and n butane exist dissolved in the petroleum Of the higher paraffins the following have been isolated.

C₅H₁₂, n pentane, dimethyl-propane, C₆H₁₄, n hexane, ethyl iso butane, C,H₁₆, n-heptane and an isomeride; either dimethyl-diethyl methane or methyl-ethyl isopropyl methane (Schorlemmer, C. J. 26, 319), C₅H₁₈, n octane and an isomeride, C₇H₂₂₂ two isomerides exist (Lemoine, Bi [2]

> a (186°) S G 4 0-742 β (180°) S G 11 0-784

41, 164)

C₁₀H₂₂, constitution not known (160°) Pelouze a Cahours, (156°) Wurtz, B1 1863, 300, (160°) SG ½ 0.753 Lemoine The solid paraffins C₂₂H₃₂, C₃₇H₃₄, and C₃₂H₃₂ have also been separated (V also Greville Williams, Tr 1857, 737, C J 15, 130, Pelouze a Cahours, A Ch [4] 1, J 1863, 410, Warren, Z 1865, 688, J 1863, 830, Warren a. Storer, Z 1868, 228, Lefebvre, Z 1869, 185, Schotlemmer, Tr 162, 111, Ronalds, Z 1865, 523, C J 18, 54, J pr 95, 421, Wurtz, A 96, 372; and for the occurrence of the same hydrocarbons in boghead coal and cannel oil, Schorlemmer, A 125, 109, Williams, A 125, 107, and for a comparative table showing the C₁₂H₂₁₊, hydrocarbons found in petroleum, or by distilling paraffin and reducing the fatty soids, Belistein, vol i 186) Warren also obtained the olefines C₁₀H₂₀, C₁₁H₂₁, and C₁₂H₂₀, from American petroleum, and traces of volatile benzene hydrocarbons and the hydro benzene compounds present in Carvasian oil have also been detected in this oil Canadian petroleum contains a somewhat gleater percentage of arc-

matic hydrocarbons, and is further characterised by its large amount of sulphur derivatives

The action of heat on American petroleum products has been studied by many observers When the crude oil is heated alone the lower members of the C_nH_{2n+2} series of hydrocarbons are evolved as gas As the temperature increases the higher paraffin hydrocarbons distil over. but at the same time vapours are evolved which are absorbable by bromine Le Bel examined this product, and found it to consist of bromides of the olefines C.H., C.H., C.H., C.H., C.H., C.H., and that there are isomeric compounds of the higher members of the series They have been separated either by fractionating the bromides obtained in this way, or by their different behaviour towards cold HCl Acetylene and crotonylene are also formed, and other less hydrogenised When the vapour of petroleum hydrocarbons ether, or the fraction (50°-80°) and containing chiefly C₂H₁₂, C₂H₁₄, and C₂H₁, is passed through a red hot tube it yields C₂H₄ and C₄H₈ and hydrocarbons absorbable by bromine These, according to Prunier, are acetylenes consisting of crotonylene C.H. and traces of C.H., C.H.,

and C₁H₁.

Petroleum spirit (70°-120°) contains the hydrocarbons C₂H₁₄, C₃H₁₆, and C₄H₁₈, and the rectified oil (150°-280°) the paraffins from C₃H₁₈. to CieHa, the crude fraction, however, contains hydrocarbons which are dissolved by sulphuric acid. The heavy oil (above 400°), used for lubricating purposes, has not been carefully ex Vaseline is the next product obtained amined on distilling the crude oil, the distillation for heavy oil being stopped as soon as acid vapours begin to be evolved. Little is known as to the constitution of its hydrocarbons When vaseline is not manufactured the distillation is continued until solid paraffin distils over The solid residue. rich in carbon, also contains hydrocarbons, and in it or in the solid paraffin have been found. besides the higher paraffins, anthracene, phen anthrene, chrysene, pyrene, chrysogen (Fritzsche, OR 54, 910), parachrysene (Rasenack), benserythrene (Schultz), and fluoranthrene (Prunier, Bi [2] 81, 298) A hydrocarbon Offic, isomeric with acenaphthalene, has also been isolated, and there are indications of the presence of quinones. From the coke Prunier and Varetine have also succeeded, by the action of solvents, in extracting small quantities of hydrocarbons containing

a very high percentage of carbon

From a green solid [190°-240°] obtained from Pittsburg, and called 'petrocene' or the 'new product,' formed by the distillation of the residue after the ordinary paraffin had come over, Prunier Isolated hydrocarbons which are called carbozene, carbonetrocene, and thallene Analysis shows that they contain 96-97 7 pc of carbon, and have formulæ, therefore, ranging from $(C_1H_2)_n$ $(C_1H_2)_n$, where n is variable but higher than 4

•Gustavson has studied the action of Al2Br. and HBr on the different fractions of petroleum ether The fraction (67°-70°), and chiefly hex-ane, gave by this treatment a solid from which he obtained an orange liquid C.H.AlBr., which decomposes above 120° and on addition of water It is insoluble in the hydrocarbons from which it is derived, and in CS2, but soluble in EtBr The other fractions give similar results, but not such a good yield

Belistem and Kurbatoff, by the action of HNO, on the fraction (95°-100°), obtained a nitro-compound C,H_{1s}(NO₂) (195°), and soluble The fraction (115°-120°) similarly ın KOH treated also gave acid nitro- products, called by

the authors trinitro isoxylene

Russian petroleum The Baku oil has been the subject of much investigation, and it appareatly is a more complicated mixture than the American product Its density, according to Mendeléeff, varies from 881-886 at 15°, and its variestion with temperature is given by the

equation
$$\frac{d\Delta}{d\mathbf{i}} = -[0\ 00635d - 0\ 0000015d^2 - 1\ 44],$$

since the co efficient of variation of density with temperature can be considered constant for any given hydrocarbon The densities d range be-

tween 750 and 900

Baku petroleum gives off a large volume of inflammable gas, and leaves on distillation a vaseline having all the properties of the American product save that its density is higher The low boiling portions of the oil contain some hydrocarbons of the C_nH_{2n+2} series, and marsh gas is evolved in the neighbourhood of the Caspian Sea, but Schutzenberger and Ionine found that the major portion of the hydrocarbons present were characterised by great inertness, and had a composition represented by the formula C_nH_{2n} , being isomerides of the olefine series of hydrocarbons The hydrocarbons were called paraffenes (C R 91, 823), and were found not to form addition products with Br, fuming HNO, nor H2SO. They found that the vapours, when passed through a red hot tube, produced aromatic hydrocarbons, and at a dull redness gave products which unite energetically with Br, and are converted into resins by H2SO, Chlorine and a little iodine convert them into unstable chloro compounds, which cannot be distilled without decomposition Of the several hydro carbons present they isolated two, (221°) and (231°), and found that the latter had a V D corresponding to the formula C14H2. Subsequent investigators have concluded that these paraffenes are the hexahydrides of the benzene series of hydrocarbons which are now called naphthenes, similar to those obtained syn-

thetically by Wreden (A. 187, 161), who described the following

 C_8H_{12} , hexahydrobenzene, SG 76 (69°); C_7H_{11} , hexahydrotoluene, SG 772 (97°); and C₆H₁₆, hexahydroisoxylene, S G 771 (117°) Beilstein a Kurbatoff have found the isomeric hexahydrometaxylene (B 18, 1820, C J 40, 159, also Markownikoff a Spady, B 20, 1850) in Russian petroleum, and subsequent investigations have established the presence of a series of naphthenes from C.H. to Markownikoff (A 234, 89-115) has also obtained similar results, and has shown that the naphthenes are the chief constituents of the oil boiling below 300° The fraction distilling (210°-330°) under 20 mm also contains a large percentage of these C_nH_{2n} hydrocarbons addition, he isolated in the fraction (85°-250°) the following aromatic hydrocarbons C_0H_0 , C_0H_0 , C_0H_1 , C_0H_1 , C_0H_1 , C_0H_1 , isoxylene, p-xylene, C_0H_1 , pseudo cumene and mesitylene, C_1oH_1 , durene, isodurene and another (diethylbenzene?), $C_{11}H_{16}$ diethyl toluene and isomerides, and hydrocarbons of the formulæ $C_{11}H_{14}$ (styrene?), $C_{11}H_{12}$, $C_{12}H_{14}$, and $C_{12}H_{14}$ Markownikoff and Oglobine, from the fraction (210°-330°) under 20 mm obtained evidence of the presence of oxygenated compounds of both acid and neutral characters (Bl [2] 41, 258), and obtained a denser naphthene C15H30 Engler has also confirmed the presence of mesitylene and pseudo cumene (B 18, 2234) ın Caucasıan petroleum (v also Le Bel, C R 103, 1017-1019)

Aschan has isolated from the Baku oil, acids of low carbon percentage derived from hexa-, hepta-, and octo naphthenes From the hepta-naphthene carboxylic acid by P and HI he has prepared an octonaphthene (117°) under 742 mm 8 G 2 0 7706, identical with that obtained by Markownikow from the Caucasian oil (B 24, 2710, and Zaloziecki, B 24, 1808) On the formation of acid compounds in petroleum v Zaloziecki, Z f Angew C 1891 410 The oil of still higher boiling-point consists

of naphthines O_nH_{2n-2} , or hydrocarbons probably derived from the naphthenes by the high temperature, together with C_nH_{2n-4} hydrocarbons and about 10 pc of true benzene comounds, which are homologues of styrene When the naphtha residues are distilled at temperatures above 400°, dissociation of the high boiling products takes place, and fresh lowboiling hydrocarbons are formed According to Lissenko a Rosenbladt, the best yield of lowboiling products is obtained at a temperature 434°-437° (Berg, J R 1887, 849), but Nobel gives 400° as the best temperature for maximum dissociation (D P J 266, 226) The Nobel brothers obtain benzene, naphthalene, and anthracene from their petroleum residues at Baku (D P J 246, 429-432) Beilstein a. 4 Kurbatoff have studied the action of nitric acid upon Russian petroleum. They find that the upon Russian petroleum fraction (95°-100°) is oxidised to succinic and several volatile acids, and at the same time a nitro compound C_cH₁₁(NO₂) (212°) is formed. The corresponding fraction of American petroleum under like treatment yields a nitro-body C,H₁₈(NO₂) (195°) The fraction gives crystals of Linitro-isoxylene The fraction (115°-120°) Markownikoff a. Oglobine isolated the above-mentioned

hydrocarbons chiefly by treating the several fractions of the oil with concentrated H.SO, and separating the sulphonates produced About 15-20 per cent of the fraction (180°-280°) is converted into these sulphonates Chiefly mono and di- acids derived from the hydrocarbons C_nH_{2n-4}, C_nH_{2n-6}, C_nH_{2n-10} and The naphthenes are not attacked by C_nH_{2n-2} G_nH_{2n-12} The naphthenes are now assumed the conc H_2SO_4 , but furning acid converts them into the principal sulphonates isolated are $C_{11}H_{13}SO_3H$, 2 isomers $C_{10}H_{13}SO_3H$, $C_{13}H_{13}SO_3H$, $C_{12}H_{12}SO_2H$, $C_{11}H_{13}SO_3H$, and $C_{12}H_{13}SO_3H$ Schutzenberger has shown that a bright red heat dissociates the low boiling naphthenes into benzene derivatives, while a dull heat determines the formation of butylene, and crotonylene and its homologues The oil obtained from Tiflis appears to be intermediate in character to that of the American and Baku products Beilstein a Kurbatoff (O J 40, 1020) isolated from samples of this petroleum, n pentane, isopentane, and a butane in the ($30^{\circ}-35^{\circ}$) fraction, a hexane and naphthenes in the ($70^{\circ}-75^{\circ}$) frac tion, and a heptane, benzene, and toluene in the (95°-100°) fraction They also obtained from this oil, by the action of HNO, a dinitro-compound $C_4H_8(NO_2)_2$ [95°] (v also Le Bel, C R 103, 1018)

The petroleum found in Germany and Galicia is characterised by a large amount of aromatic hydrocarbons, and Kraemar a Bottcher hold that the hydrocarbons of German petroleum and Baku oil differ from coal tar and shale tar oils only in the relative proportions of those hydrocarbons which are attacked by conc H.SO, and HNO, (B 20, 595-609)

Engler has made a very systematic investiga tion into the composition of the German oils, and has isolated or identified the following sub stances gases CH₄, CO, CO₂, N, C,H₄, and homologues, in the first fraction (below 150°) C_5H_{12} , C_6H_{14} , and C_9H_{20} , in the fraction (160°-182°) pseudo-cumene and mesitylene, and in the higher-boiling portion solid paraffin The oil from Oelheimer and Wietzer contains saturated hydrocarbons, naphthenes, but no solid paraffin nor volatile products below 150° The Tegernnor volatile products below 150° see oil is especially rich in aromatic hydrocarbons (Engler, D P J 267, 550-570, 592-597, 268, 76-90) Engler has also detected phenols and fatty and oleic acids in many specimens Boussingault has also isolated from Alsatian petroleum, petrolene, and a black colouring mat ter similar to that found in Alsatian bitumen and in Galician oil (Le Bel, Bl 1888, 359)

GALICIAN PETROLEUM contains hydrocarbons of the C_nH_{2n+2} and C_nH_{2n-6} series (Freund, A 115, 91) It has also been examined by Lacho of the Calling 12 of 18 toluene, xylene, and mesitylene, but no olefines From the high S G of the benzene fractions he also infers the presence of naphthenes (hexahydro toluene and hexahydro isoxylene) lewski has also found 2 p c of aromatic hydro carbons, principally benzene and p xylene, in Galician oil According to Bandrowski, this

petroleum contains a small quantity of a basic body resembling the alkaloids (M 8, 225), and Weller has also detected the presence of bases in the yellow oil (S G 85) obtained from Saxon petroleum (B 20, 2098) On the Galician petro leum industry v Redwood, S C I 1892

BURMESE PETROLEUM has only been in verfectly examined Romanis has found gases, benzene, and solid paraffin in the crude oil and 5 p c of solid paraffin in that refined at Rangoon solidifies at 24°, and has a SG 85-9 From another district in Burma (Arracan) a mineral oil is obtained which contains benzene and its homologues, but does not solidify also lower, 825 (C N. 59, 292) Its SG 1s

The origin of petroleum—Mendeléeff has given considerable attention to this subject, and has advanced strong reasons for believing that mineral oils have not been produced like coal from the decomposition of past vegetation believes that it is formed in the depths of the earth beneath the very site on which it is found, since it cannot be water borne The absence of any large masses of organic matter in the oil districts negatives the vegetable origin of petro In Europe the oil wells belong to Ter tiary and late geological periods, but in America and Canada the oil bearing sands are found in the Devonian and Silurian formations, and hence below the carboniferous beds The oil beds also always run parallel to mountain ranges, and Mendeléeff believes that water has found its way through the fissures formed at the upheaval of these ranges to the heaten metallic carbides below, resulting in the formation of metallic oxides and hydrocarbons, the chemical composition of which depends upon the conditions of temperature and pressure under which they are formed This origin of petroleum is supported by the frequent presence of sulphur in crude oils, by the asphaltene containing a mineral ash consisting of oxides of Fe, Al, Cu, Ca (Ag), and by the non saturated nature of many of the hydrocarbons The occurrence of petroleum in the lavas of Etna lends additional support to this theory (Silvestri, G 1877, 1) Hoefer, Engler, Leopold v Buch, Sterry Hunt, and many geologists believe that petroleum has been formed by the decomposition of organic matter of animal origin, and advance the presence of nitrogen compounds and direct experiments with animal fats in support of their view the origin of petroleum see Neues Wörterbuch, m 39, Byasson (M S 1876, 1077), Mendeleeft (Revue Scientif 1877, 409), Anderson (B A address, 1889), Engler (B 21, 1816-1827), Hoefer 'Mineralohndustrie' in Bolley's Technologie), Zaloziecki (D. P. J. 280, 69, 85, 188), Watson Smith (S C I 10, 979)

PETROLEUMIC ACID v HENDECENOIC ACID PETTENKOFER'S REACTION A blood red colour on warming with cane sugar and conc H2SO4 The colour is produced by the bile acids, cholic acid, and many other bodies aldehyde may be used instead of sugar (Mylius, H 11, 492, v also vol 1 p 508)
PEUCEDANIN v IMPERATORIN

PEWTER An alloy of Pb and Sn; v this

vol p 125 PHACONIN v PROTEIDS PHASEOMANNITE v INOSITE **PHASOL** $O_{15}H_{24}O$ [190°] $[\alpha]_D = 30$ 6° in a 4 p c chloroform solution. Found in the husks of peas (Pisum sativum) (Likernik, B 24, 188) Groups of tables (from alcohol), insol water, v sol hot alcohol and ether Gives a purple colour on shaking its chloroform solution with H2SO. of 8 G 17

PHELLANDRENE A dextrorotatory modification of this terpene occurs in oil of elemi, a lævorotatory variety in Australian eucalyptus oil (Wallach, A 246, 234) The dextrorotatory variety occurs also in the seeds of Phellandrium

aquaticum, and in oil of fennel (v Terffnes)
PHENACETURIC ACID C1,H1,NO., 20
CH,Ph CO NH CH CO2H [143°] S 7 at 11° Occurs in horses' urine (Salkowski, B 17, 3010) Found in urine after taking phenyl acetic acid (Salkowski, H 7, 162) Prepared by digesting phenyl acetic anhydride with glycocoll and benzene (Hotter, J pr [2] 38, 97, B 20, 84) White lamins (from water) or cubes (from On nitration it gives p nitro phenace-[173°] —CaA', 2aq S (of CaA',) 3 at alcohol) turic acid [173°] —CaA', 2aq S (of CaA',) 3 at 11°—CuA', aq —AgA' amorphous insoluble pp

Methyl ether MeA' [86 5°] Needles Ethyl ether EtA' [79°] Prisms n Propylether PrA' [319] Plates Amide [174°] Pearly tables

PHENACONIC ACID A name given by Carius to a mixture of maleic and fumaric acids

PHENACYL The radicle C₆H₅ CO CH₇
DI PHENACYL ACETIC ACID v DI BENZOYL-ISOBUTYRIC ACID

DI-PHENACYL-ÄCETOACETIC ETHER

(CH,Bz), CAc CO, Et [83°] Made from acetoacetic ether, NaOEt, and phenacyl bromide (Paal a Hoermann, B 22, 3225) Monoclinic crystals, sl sol cold alcohol, v sol CS Alco holic NH, at 125° forms two bodies [136°] and [192°]

Mono-oxim [63°] Fla Di oxim [63°] Flakes Flakes [68°] Flakes Tri-oxim

Di-phenyl di hydraside C, H, N, O, [880-920] From the ether and phenyl hydrazine PHENACYL-o-AMIDO BENZOIC ACID

Formyl derivative CH,Bz N(ČHO) C,H, CO,H [184°] Got by oxidising quinoline phenacylo bromide with KMnO₄ (Bamberger, B 20, 3342) Tables (from alcohol), sl sol cold water

PHENACYLAMINE C.H. CO CH.NH. w Amido acetophenone Got by decomposing phenacyl phthalamic acid [160°] with conc HClAq (Goedeckemeyer, B 21, 2687) Converted by NH, into di-phenyl pyrazine -B'HCl [188°] —B'₂H₂PtCl₆ 210°] -B'C,H,N,O, [c [175° Yellow needles

PÄENACYL ISOAMYL MALONIC ACID C_0H_1 CO CH_2 $C(C_0H_1)(CO_2H)_2$. [160°] Made from sodium isoamyl malonic ether and phenacyl bromide, the product being saponified (Paul a Hofmann, B 23, 1500) Needles, v sol alcohol Yields CH,Bz CH(C,H₁₁) CO₂H [103°] on heating —NH,C₁₆H₁₉O₄ [165°] Needles. Ethyl ether Et,A" Oil

Amide Crystalline
PHENACYL-BENZOYL ACETIC ETHER Crystalline

OH, Bz CHBz CO,Et Dr - bensoyl - propionic ether [c 58°] Made from w-bromo aceto phenone and sodium benzoyl-acetic ether (Kapf

a Paal, B 21, 1485, 8053) Crystals (from ether), insol water With aqueous potash it gives benzoyl propionic acid, while alcoholic potash yields CPh C CHBz CO₂H [185°] and CH₂Bz CH₂Bz [145°]

PHENÁCYĽ BROMIDE v w BROMO ACETO-PHENONE

PHENACYL CHLORIDE v .- CHLORO ACETO-

PHENACYL CYANIDE v BENZOYL-AGETO

DI-PHENACYL-MALONIC ACID v DI BEN ZOYL DI METHYL MALONIC ACID

PHENACYL PHTHALAMIC ACID

CO₂H C₆H₄ CO NH CH₂CO C₆H₅ [160°] Made by the action of alcoholic potash on phenacylphthalimide (Goedeckemeyer, B 21, 2686) Needles, insol water Decomposed by boiling water Decomposed by boiling HClAg into phthalic acid and amido acetophenone

Phenacyl-phthalimide C.H. C.O. N CH2Bs [167°] Made by heating w-bromo acetophenone with potassium phthalimide at 150° (Goedeckemeyer, B 21, 2685) Dimetric plates, sol alcohol and ether, almost mosol water and ligroin

Phenyl-hydrazide C₅H₄O₂ N CH₂ C(N₂HPh) C₅H₅ needles, insol water [155°] Orange

PHENACYL SULPHIDE S(CH, CO C,H,), [77°] Made by adding ω bromo acetophenone (100 pts) in alcohol (400 pts) to a solution of Na (12 pts) in alcohol (400 pts) saturated with H₂S (Tafel a Moritz, B 23, 3474) Prisms (from hot alcohol) Reduces Fehling's solution Yields a di oxim [151°] and a diphenyldihydrazide [147

PHENACYL SULPHOCYANIDE

C₆H₅ CO CH₂ S CN Sulphocyanoacetophenone [74°] Made by mixing alcoholic solutions of barium sulphocyanide and w bromo acetophenone (Arapides, A 249, 10) Needles or prisms, v sol ether, insol water Hot HCl converts it into CH.Bz S CONH, and finally oxy phenylthiazole

PHENACYL THIOCARBAMATE

CH Bz S CONH. A very unstable body got by boiling phenacyl sulphocyanide with conc HClAq until crystallisation begins (Arapides, A 249, 12) Yields oxy phenyl thiazole on boiling with HClAq—B'HCl [c 177°] Silky needles— HClAq —B'HCl [c 177°] Silky needles — B',H PtCl, [c, 200] Yellow crystalline powder

PHENACYL TOLUIDINE v TOLYL-AMIDO-ACETOPHENONE

Di phenacyl p-toluidine C.H.Me N(CH2Bz)20 Formed from p toluidine and ω -bromo acetophenone in alcohol (Lellmann a. Donner, B 23, 168) Needles, v sol alcohol

PHENAMYLAMINE v AMIDO-AMYL-BENZ-

Diphenamylamine NH(CoH, CoH11)2. isoamyl di phenylamine

amyl di phenylamene (320°)
Formed, together with amido isoamyl-bens. $C_6H_4(C_5H_{11}) NH_2$ (260°) by heating C.H.(C.H.1) OH with ammoniacal ZnBr, or with ZnCl, and NH,Br or NH,Cl, the yield being 18 to 25 pc (Lloyd, B 20, 1257) —B',H.PtCl.

Acetyl derivative NAc(C11H11)2 White glistening plates
PHENANTHRAQUINONE C14H.O. 16

C'H'CO or C'H'CO Mol. w. 208 [202°] (Hayduck, A 167, 184) (above 860°) Formed by oxidising the residue left after evaporating the alcoholic washings from the distillate got in preparing anthracene from o bromo benzyl bromide and Na (Jackson a White, Am 2, 392)

Preparation—1 By warming phenanthrene (1 pt) with K₂Cr₂O₇ (1 pt), water (3 pts) and H₂SO₄ (1½ pt) and crystallising the product from diluted HOAc (Fittig a Ostermayer, B 5, 938, A 166, 365)—2 By adding a solution of CrO₄ in HOAc to a hot solution of phenanthrene in HOAc (Graebe, B 5, 861, A 167, 139) The product is purified by solution in aqueous NaHSO₅ followed by ppn with HOI and crystallisation from HOAc—3 By oxidising crude phenanthrene (310°-340°), the following bodies being obtained at the same time, methyl anthraquinone, diphenic acid, carbazole, acridine, and diphenylene-ketone (Anschütz a Schultz, A 196, 32)

Properties - Orange needles or prisms (from solvents) or tables (by sublimation), almost mad cold water, at sol hot water and cold alcohol, m sol hot alcohol, ether, HOAc, and Conc H₂SO₄ forms a dark green solution but does not sulphonate it, even at 100° A solution of phenanthraquinone (1g) in HOAc (20 cc) mixed with toluene (4 cc) containing methyl-thiophene gives on shaking with H2SO (16 cc) a bluish-green liquid which, when poured into water and extracted with ether, imparts a purple colour to the ether (Laubenheimer, B 8, 224, V Meyer, B 16, 1624) The colouring matter $C_{10}H_{12}SO$ formed in this reaction gives anthraquinone on distilling with PbCrO₄ (Oderheimer, B 17, 1338) A solution of phenanthraquinone in wet ether when exposed in closed tubes to direct sunshine is readily re duced to phenanthrahydroquinone, with formation of aldehyde (Klinger, B 19, 1869)

Reactions -1 Oxidised by chromic acid to diphenyl di-o-carboxylic acid — 2 Alkaline KMnO, gives oxy-diphenylene acetic acid and diphenylene-ketone (Anschutz a Japp, B 11, 212) -8 Reduced to dihydride by warming with aqueous SO₂ -4 Sodrum-amalgam acting on its alcoholic solutions forms diphenic acid [226°] (A a S) -5 Boiling aqueous NaOH yields $C_{12}H_6$ C(OH) CO₂H (A a J) Boiling barytawater forms, besides oxy-diphenylene acetic acid, diphenylene ketone and fluorene alcohol -6 Alcoholic potash gradually forms diphenic acid, the solution meanwhile giving out phosphorescent light on shaking (Lachovitch, B 16, 382) -7 By passing the vapour over heated lead oxide di phenylene ketone is formed (Wittenberg a Meyer, B 16, 502) -8 Distillation with dry soda-lime gives diphenyl When the soda-lime is moist, fluorene, fluorene alcohol, and diphenylene ketone are also formed —9 Distillation with quick-lime gives fluorene and diphenylene ketone (Anschütz a. Schultz, B 9. 1400).-10 Distillation with sinc-dust yields phenanthrene —11 An ethereal solution of ZnEt, decolourises it On adding alcohol, boiling, and filtering, crystals of O, H, O, HOEt, [77°], are formed. These are rectangular plates, insolventer Ac₂O converts it into $C_{18}H_{12}O_{2}Ac$, $[108^{\circ}]$ (Japp, O J 85, 526) —12 With POl, it gives $C_{6}H_{4}$ COl, benzene may be used as diluent. The

product 'di-chloro-phenanthrone' may be re crystallised from benzene It melts at [165°], although at 140° it begins to get brown Alkalis convert it into phenanthraquinone Shaken with alcoholic potash, it is oxidised to diphenic acid, the solution phosphorescing meanwhile Iron and acetic acid reduce it first to chloro phenanthrone, C.H. CHOI [123°], and then to phenanthrone C.H. CH. CH. (149°) Chloro C.H. CO., [149°] Chloro phenanthrone may be recrystallised from glacial acetic acid, and is not decomposed even by borling alkalis, but HNO. (S G 18) converts it into nitro phenanthraquinone Phenanthrone may be phenanthraquinone crystallised first from glacial acetic acid, then from butyl bromide (B Lachovitch, J pr [2] 28, 168) -18 By exhaustive chlorination with SbCl, it yields perchloro-diphenyl together with a very small quantity of per chloro benzene (Merza Weith, B 16, 2870) —14 Benzoic alde hyde (free from HCy) at 260° forms benzalquin of phenanthrene C₃₅H₂₄O [329°], which crystal lises from CS, in rectangular plates and yields benzoic acid and phenanthraquinone on oxida tion It gives off no gas with ZnEt2, hence contains no hydroxyl (Japp a Wilcock, C J 37, 661) — 15 Heating with PCl, followed by addition of water forms C.H. C(OH) PO(OH)₂ crystallising in flesh coloured plates, sol water, alcohol, and ether (Fossek, M 7, 36)—16 Acctone at 200° forms acetone phenanthraquinone $C_{1}H_{1}O_{2}$ (vol 1 p 33) By the auton of $H_{2}SO_{4}$ on this body a small quantity of $C_{3}H_{2}O_{2}$ [238°] is formed (Wadsworth, C J 59, 105) -17 Ammonia passed into an alcoholic solution forms phenanthraquinonimide C14H9NO On heating with alcoholic NH, in sealed tubes there are formed diphenanthrylene azotide $C_{28}H_{16}N_2$, two compounds $C_{28}H_{16}N_3O$ [282°] and [over 300°] and a compound $C_{14}H_{16}N_2$ [above 285°] (Schmidt, B 7, 1365, Anschutz a Schultz, A 196, 49, Zincke, B 12, 1641, Sommaruga, M 1, 146, Japp, C J 49, 845, 51, 98)—
18 Bensow aldehyde and aqueous NH, at 100° quickly forms C21H12NO or C12H2 C2 O CPh This 'benzenyl amido phenanthrol' crystallises from benzene in tufts of silky needles, [202°], v sl sol alcohol, sol cone HClAq and cone H,SO It yields benzoic acid and without change phenanthraquinone on oxidation HClAq at 200° forms benzoic acid It does not act on ZnEt. (Japp, C J 87, 666, 89, 225) —19 Cuminic aldehyde and NH. forms, in like manner, cumenyl- $C_{14}H_{6} < \stackrel{O}{\sim} C C_{6}H_{4} C_{8}H$ amido - phenanthrol [186°], crystallising from benzene ligroin in silky needles, and forming in conc H.SO, a yellowish green fluorescent liquid (Japp a Wilcock, C J89, 226) -20 Furfuraldehyde and aqueous NH, give $C_{14}H_{4} < \stackrel{O}{N} > C C_{4}H_{4}O$ [281°], orystallising from isosmyl alcohol in needles (J a W)— 21 Sahcylic aldehyde (1 mol) and conc NH,Aq form, on warming, o oxy benzenyl diamido - phenanthrene C,H, C NH C C,H, OH This body (Japp a Streatfeild, C J 41, 146) crystallises from HOAc in slender needles [270°-

276°], and is sl sol alcohol, v sol HOAc dissolves in boiling KOHAq, and is ppd by CO2 Boiling alcoholic potash gives salicylic acid HClAq at 200° has no action BzCl yields a benzoyl derivative [220°] —22 o-Methoxy beazoic ald hyde (15g) heated with phenanthra quinone (30%) and excess of NH, Aq at 100° deposits yellow crystals of C14H, N2H C C6H4OMe [208°], while the mother liquor contains C₁₄H₈<0 O C₈H₄OMe, which crystallises in white needles, v sol hot benzene (Japp a Streat feeld, C J 41, 154) -23 p Oxy benzoic aldehyde and aqueous i'H form p oxy benzenyl-di amido phenanthrene [abive 350°], crystallising from HOAc in slender needles It yields an acetyl derivative [205°-210°] (J a S) -24 Aldehyde ammonia yields an amorphous base (J a W) -25 Alcoholic methylamine forms, on warming, yellow crystals The mother liquor deposits C₁₆H₁₄N₂ or C₁₄H₈(NMe)₂, crystallising in colour-less prisms [186°], and yielding B'HCl, v sol water, and B'HNO₃, B'_.H₂SO₄, B'_{.2}H₂C_.O₄, all crystallising in needles (Zincke, B 12, 1643) — 26 Ethylene diamine and HOAc form the azine $C_{14}H_8 < N > C_2H_4$, which crystallises from alcohol in needles [181°] in needles [181°] It yields a platinochloride B'₂H₂PtCl₆, nearly insol alcohol (Mason, B 19, 112, 20, 268)—27 Propylene diamine yields C₁,H₁₂N₃, crystallising in needles [128°], and yielding B',H₂PtCl₂ (Strache, B 21, 2362) yielding B' H₂FtU₁, (Suradio, 28 Trimethylene dratnine forms C₂₈H ,NO₂, a rest melted at 250° Its lemon yellow powder, not melted at 250° alcohol solution is coloured violet by acids 29 Tetra amido phenazine and HOAc give $C_{14}H_{8} < N > C_{8}H_{2} < N > C_{8}H_{2} < N > C_{14}H_{8}$ a green crystalline pp, forming a bluish green solution in H2SO4, changing on dilution through red to orange (Nietzki a Muller, B 22, 450) Phenylene o diamine gives phenanthrazine $C_{14}H_6 < N > C_6H_4$, [217°], insol water, v sol

alcohol (Hinsberg, A 237, 340) -31 Tolylene-odiamine forms $C_{14}H_{8} < N > C_{0}H_{3}Me$ [213°] -32 Heating with acetamide and HOAc forms the azine $C_{14}H_s < N > C_{14}H_s$, crystallising in yellowish brown flat needles, [400°], sol aniline, nitro benzene, and phenol (Mason, C J 55, 108) - 33 Naphthylene (1,2) - diamine yields $C_{14}H_{6} < N > C_{10}H_{6}$ [264°] (Leuckart, B 19,174) — 34 Phenyl - naphthylens - (1,2) dramine boiled with HOAc and phenanthraquinone forms, on adding-HNO, a pp of $C_{bo}H_{10}(NO_{s})N_{s}O$, whence boiling potash separates $C_{14}H_{s}\langle NP_{h}(OH)\rangle$ which forms a yellow solution in ether It forms a blue solution in H₂SO, turned orange by dilution (Witt, B 20, 1185) -85 Netro-ophenylene-diamine and HOAc give, on heating, $C_{2a}H_{11}N,O_{2}$ [251°] (Heim, B 21, 2301) — 36 Isobutyl phenylene-diamine in HOAc forms C, H, N, O, H, C, H, [147°], crystallising in pale-nellow needles, coloured cherry red by H.SO. (Gelzer, B 20, 3253, 21, 2951) The compound C, H, N, C, H, Br C, H, [1546] also

It forms yellow needles (3) Isobutyl phenylene-damme gives an isomeric azine [144°]—
in damme gives an isomeric azine [144°]—
in damme (6,4,2,1) Bromo tolylene damme in HOAc forms C_{1,}H_s N₂ C_sH_sMeBr [210°] crystallising in yellow needles (Hartmann, B 23, 1050)—
38 i. Tri amido benzene (from chrysoidine) yelds C_{1,}H_s N₂ C_sH_sNH_s as brown crystals in in the control of the cont

Combinations — C₁₄H₂O₂NaHSO₂2aq Small colourless plates, v e sol water, which slowly decomposes it — (C₁₄H₂O₂),HgCy₂ [223°] Red crystals with green lustre, deposited from a hot saturated solution of phenanthraquinone and HgCy₂ in acetone (Japp a Turner, C J 57, 7) — (C₁₄H₂O₂),HgCl₂ [223°] Red prisms (from boiling acetone) — C₁₄H₂O₂ZnCl₂ Dark reddishbrown needles got by adding a hot solution of ZnCl₂ in HOAc to a hot solution of phenanthraquinone in HOAc (Japp a Turner, C J 57, 5)

quinone in HOAc (Japp a Turner, C J 57, 5)

Hydrocyanide C₁₁H₂O₂(HCN)₂ tufts of needles, formed by action of 30 pc HCN solution Decomposed by heat into its components Conc HCl decomposes it, giving off CO₂ and forming C₁₅H₂NO [241°] and C₁₅H₁₁NO₂ [183°]

The latter separates from benzene in slender needles Both dissolve in sodium carbonate, expelling CO₂, the compound [241°] producing C₁₅H₂NO₂ 4aq, and also the corresponding C₁₅H₂NO₂). Ba 7aq whence HCl liberates C₁₅H₂NO (Japp a Miller, C J 51, 29)

CH, CNOH Mono oxim C14H2NO se [158°] Formed by boiling phenanthraquinone with alcoholic hydroxylamine hydrochloride for an hour (Goldschmidt, B 16,2178) Small yellow needles, v sol hot alcohol Forms coloured pps with metallic salts (Kostanecki, B 22, 1347) Boiling NaOHAq forms a green liquid Conc H.SO, forms a blood red solution and at 100° converts it into diphenylene ketone carboxylic amide HCl, Ac,O, and HOAc at 100° convert it, by intra molecular change, into a weak base [217°], probably C.H. CONH, and also form prisms [92°] (Wegerhoff, A 252, 17) Ac,O forms C₂₈H₁₈N₂O crystallising in small brownish tables [247⁵] nearly insol alcohol and ether (Zincke)

Dt oxim C.H. C NOH [202°] Formed by heating an alcoholic solution of phenanthraquinone (1 mol) with hydroxylamine hydrochloride (4 mols) for 30 hours at 100° (Auwers a V Meyer, B 22, 1993) Minute yellow prisms (from alcohol or HOAo), insol water, sl sol hot alcohol and ether Cone H.SO, forms a bloodred solution NaOHAq forms a yellow solution, depositing the Na salt as pearly plates Alcohol at 150° forms the anhydride C.H. C N. (188°] which crystallises H long yellow needles, insol. NaOHAq A solution of the dioxim in HOAs

and Ac.O saturated with HOl in the cold gives the acetyl derivative C.H. C NOAc separating

from alcohol in minute crystals [184°]

Phenyl-hydraside CmH1.N2O [165°] Formed by warming an alcoholic solution of phenanthraquinone with aqueous phenyl-hy-drazine hydrochloride (Zincke, B 16, 1564) Red needles or plates (from alcohol) Gives a violet solution in H2SO

Di bromo-phenanthraquinone C, H, Br₂O₂ [280°] (H), [283°] (Ostermayer, B 7, 1090) Made by heating the quinone with Br and a little water for six hours at 180° (Hayduck, A 167, 185) Yellow nodules (nom alcohol Yields di bromo diphenyl dicarboxylio

Nitro-phenanthraquinone

[1 2]C,H, ——CO [1 4 2]C,H,(NO₂) CO [257°] Formed from the quinone and boiling HNO, (SG 14) (Anschütz a Schultz, B 9, 1404, Strasburger, B 16, 2346) Orange plates (from HOAc) yields nitro diphenyl dicarboxylic acid [217°] on oxidation By oxidation of (a)-, (β) , and (γ) nitro phenanthrene with CrO₃ and HOAc there are formed (a)-, (β) -, and (γ) nitro-phenanthraquinones [215°-220°], [260°-266°], and [263°] respectively (Schmidt, B 12, 1156)

Nitro-phenanthraquinone [282°] Made by warming chloro-phenanthrone with nitric acid (S G 1 3) (Lachovitch, J pr [2] 28, 172) Orange

plates, sl sol HOAc Di nitro phenanthraquinone

 $C_0H_3(NO_2)$ CO $C_0H_3(NO_2)$ CO $C_0H_3(NO_2)$ CO $C_0H_3(NO_2)$ CO $C_0H_3(NO_2)$ Made by boiling phenanthrene with fuming HNO₃ or with a mixture of HNO, and H2SO, Obtained also, together with a more soluble isomeride, by nitration of phenanthraquinone and of nitro phenanthraquinone [257°] (Graebe, A 167, 144, Schultz, A 208, 108, Strassburger, B 16, 2346) Yellow plates, v sl sol alcohol Yields di nitro diphenyl dicarboxylic acid [253°] on oxidation

Amido-phenanthraquinone

[1 2]Ç₆H₄-[c 200°] Formed by re-[1 4 2]0,H,(NH,) ČO duction of nitro-phenanthraquinone [257°] with tin and HCl (Anschutz a Meyer, B 18, 1943) Violet-black needles, sl sol hot water, forming a reddish violet solution -B'HCl yellowish red feathery needles

Di amido phenanthraquinone

[1 4 2]C₆H₂(NH₂) CO [1 4 2]C₆H₂(NH₂) CO Formed by reduction of the di nitro-compound with tin and HCl (A a M Kleemann a Wense, B 18, 2168) Violet black needles, not melted at 310° The hydrochloride forms yellow plates.

C₆H₄——CO C₆H₂(OH) CO Oxy-phenanthraquinone Formed by the action Phenanthrolgumone of nitrous acid on amido phenanthraquinone Brownish red needles May be sublimed. Forms

a yellowish-green solution in NaOHAq

Acetyl derivative [200°-210°] JI-oxy-phenanthraquinone $O_{14}H_0(OH)_2O_3$. Formed by the action of nitrous acid on diamido-phenanthraquinone (A a M.) Minute dark-brown needles Vialde (A) orystallising in yellowish-red needles.

Hydro phenanthraquinone C14H10O2 C'H'COH Phenanthragumone dihydride C.H. COH Phenanthrenehydrogunone Mol w 210 Formed by heating phenanthraquinone with aqueous SO2, or by passing SO2 into a warr alcoholic solution of the quinone (Graebe, A 167, 146) Colourless needles, m sol hot w ter, v e sol alcohol, ether, and benzene Absorbs oxygen when moist, or in aqueous solution, forming the quinhydrone C₂₈H₁₈O₄, which crystallises in black needles [169°], and finally phenanthra FeCl, HNO, and CrO, oxidise it in aumone the same way

Mono acetyl derivat se C₁₄H₈(OH)(OAc) [170°] Got by boiling phenanthraquinone with HOAc, HI, and red P (Japp a Klingemann, C J Proc 6, 31) Formed by the action of sunlight on phenanthraquinone in aldehyde (Klinger, A 249, 138) Flat needles

derivative C14H8(OAc)2. Dr-acetyl [202°] Formed from the dihydride and Ac.O Colourless plates (from benzene), not oxidised by boiling chromic acid mixture Not attacked by heating with KOHAq, unless the solution has a higher SG than 13

Benzoyl derivative $C_{14}H_8(OH)(OBz)$ [178°] Got by action of sunlight on phenanthraquinone and benzoic aldehyde (K) White needles (from HOAc)

Valery l derivative C1. H8(OH)(O C. H9O)

[149°] Got by using isovaleric aldehyde

Ethyl derivative C, H, (OH) (OEt) On treatment of phenanthraquinone with ZnEt and alcohol successively the compound C_{1e}H_{1e}O₂EtOH [77°] is got, from which EtOH can be removed by standing for some months m vacuo over H₂SO₄ (Japp, C J 37, 408) a mono acetyl derivative C₁₆H₁₅AcO₂ [103°]

Isomeride of hydro phenanthraquinone $C_{14}H_6(OH)_2$ [143°] Got by heating its diacetyl derivative with alcoholic NH₃ (Fischer a Ge richten, B 19, 792) Needles, very oxidisable, its alkaline solution turning green and finally red

Acetyl derivative C14H8(OAc), Made by boiling morphine methylo iodide with Ac₂O, adding dry AgOAc, filtering, and heating the filtrate at 180° Needles (from ether)

Di amido-hydro phenanthraquinone C14H6(NH2)2(OH)2 Formed by reduction of di nitro phenanthraquinone with SnCl2 (Kleemann a Wense, B 18, 2168) Very readily oxidised by air, FeCl, or CrO, to violet black needles of diamido phenanthraquinone —B"H2Cl23aq

Tetra-acetyl derivative C₁₄H₆(NHAc)₂(OAc)₂. Colourless needles, solid at 800°, sl sol alcohol and HOAc

Phenanthraquinone carboxylic acid

C₂H₄ CO₂H) CO [815°] Made by oxidation of phenanthrene carboxylic acid with CrO, in HOAc (Japp a Schultz, B 10, 1661, A 196, Orange substance, sol NaHSO Aq

Phenanthraquinone sulphonic acid C₁₄H₇(SO₃H)O₃ Formed quinone and SO₃ (Graebe) Formed from phenanthraquinone and SO, (Graebe) Gives a colouring matter resembling alizarin when fused with potash.

Phenanthrone C₁₄H₁₀O [149°] Formed as above (*Reastion* 12). Brownish red plates, v.s

tol alcohol and ether, does not combine with NaHSO, Its alkaline solution is green

Diphenanthrylene azotide C14H, N2 C14H, [above 400°] Formed from phenanthraquinone and alcoholic NH, at 100°, and also by heating terrapheny usine with soda lime to a red heat (Japp a Bu. on, C J 49, 845, 51, 98) erystalline powder or yellow needles (by sublimation), v sl sol ether Its solution in H.SO. is deep blue, becoming orange on dilution

Isophenanthraquinone $C_{14}H_8O_2$ [156°] Formed by the further action of CrO, and HOAc on an oil formed in the oxidation of phenanthrene, which remains in the alcoholic liquid from which phenanthraquinone has separated (Hayduck, A 167, 185) Yellow crystals (from alcohol), sl sol water, v sol hot alcohol

PHENANTHRAZINE v PHENANTHRAQUINone, Reaction 29

PHENANTHRENE C14H10 16

[1 2] C.H. CH [1 2] C.H. CH Mol w 178 [100°] (Graebe, Schiff), [103°] (Reissert, B 23, 2244) 1 V) S (alcohol) 2 62 at 16°, 10 08 at 78° (toluene) 33 at 16 5° (Bechi, B 12, 1978) SVS 167 05 (Schiff) SV 1862 (Lossen, A 254, 54), 1967 (Ramsay) H.F. (from diamond) -39,400 (Berthelot a Vieille, A Ch [6] 10,446, Berthelot a Vieille, A Ch [6] 10,446, - 33,400 (Bettielle a vielle), 2 (R 5), 2, 3, 3, 40 (Bet), 3, 2 (R 5), 40, 44, 44, 46 (B a V), 1,692,000 (S) HCp 1,700,400 (B a V), 1,693,500 (S) Occurs in coal tar cl (Graebe, B 5, 861, A 167, 181, Fittig a Ostermayer, B 5, 933, A 166, 361, Hayduck, B 6, 532, A 167, 177) and in 'idryl' got by distillation of an Idrian ore of mercury

Formation.—1 Together with toluene by passing s di phenyl ethylene through a red hot tube (Graebe) -2 From s di phenyl ethane, from toluene (Graebe, B 7, 48), from a mixture of diphenyl and ethylene, from di methyl di phenyl, and from phenyl tolyl methane (Barbier, C R 79, 121) by passing the vapours through Other hydrocarbons are also red hot tubes formed in these reactions -3 Together with anthracene in the action of sodium on [12] C, H, Br CH2B1 (Jackson a White, Am 2, 391) -4 By heating coumarone and benzene to a high temperature (Kraemer a Spilker, $B \ge 3$,

Preparation - By fractional distillation of the portion of hydrocarbons (310~360°) from coal tar oil, followed by crystallisation from al cohol A solution of crude phenanthrene (3 pts) in hot toluene mixed with picric acid (1 pts) deposits on cooling the picric acid compound in golden needles, which may be subsequently de composed by alkalis The mixture of phen anthrene and anthracene may also be crystallised from toluene, when anthracene separates first (Wense, B 19, 761) Chromic acid mixture attacks anthracene more readily than phen anthrene, so that a small quantity of anthracene may be removed by its means (Anschutz a Schultz, A 196, 35)

Proper ies — Small colouriess plates (from alcohol), si sol cold alcohol, v sol ether, benz ne, HOAc, and CS, May be sublimed Exhibits slight blue fluorescence lts absorption spectrum in the ultra-violet has been studied

by Hartley (C J 39, 164) Not reduced in alco-

holic solution by sodium amalgam
Reactions —1 Oxidised by chromic acid mixture and by CrO, in HOAc to phenanthra-quinone—2 HIAq and P at 200° form a tetra hydride -8 Bromine added to its solution in ether or CS2 forms unstable C14H10Br, crystallis ing in four sided prisms (F a O , Hayduck, A. 167, 180) This dibromide melts with effervescence at 98°, and its alcoholic solution gives app of AgBr on adding AgNO, By alcoholic KCy it is reconverted into phenanthrene (Anschutz, B 11,1217) —4 By exhaustive chlorina tron with SbCl, it yields per-chloro benzene (Merz a Weith, B 16,2869)

Combinations —C₁₄H

₁₀C₆H

₂N

₃O

₄ [143°]

S (95 p c alcohol) 2 7 at 15° Golden prisms — $C_{14}H_{10}C_{8}H_{3}Cl(NO_{2})_{2}[1\ 2\ 4][44^{\circ}]$ Orange needles (Willgerodt, B 11, 604) $-C_{14}H_{10}C_{8}H_{2}Cl(NO_{2})_{3}$ ſ88°1 Lemon yellow needles (Liebermann, B 8, 378)

 $Tetrahydride C_{14}H_{14}$ [0°] (310° 1 V) SG 12 1 067 Got by reducing phenanthrene with HIAq and P, or by isoamyl alcohol and sodium (Bamberger a Lodter, B 20, 3076) Liquid, v sol hot alcohol Yields phenanthra quinone on oxidation by CrO, and HOAc

Octohydride C14H18 (below 300°) Got by heating phenanthrene with HIAq and P at 240° (Graebe) Liquid

Perhydride C₁₄H₂₄ [-3°] (270°-275°) SG 2° 933 Made, together with a hydride (290°), by heating phenanthrene with HIAq and red P at 250° (Liebermann a. Spiegel, B 22, 779) Yields phenanthrene and anthracene when distilled with zinc dust. Not attacked by H2SO., HNO₃, or Br

Chloro phenanthrenes By passing chlorine onto phenatures by passing enterine into a solution of phenanthrene in HOAc the compound C₁₄H_aCl_e [170°] is formed, together with oily C₁₄H_aCl and C₁₄H_aCl_e Alcoholic potash converts C₁₄H_aCl_e into C₁₄H_aCl_e By heating phenanthrene with SbCl_e the compounds C₁₄H_aCl_e [172°], C₁₄H₄Cl_e [250°], and C₁₄H_aCl_e [270°–280°] may be obtained (Zetter, B 11, 165), the final products having C [1] and C [1]. the final products being C.Cl. and CCl.

Bromo phenanthrenes Bromine acting on phenanthrene dissolved in ether forms C14H10Br2, which at 100° splits up into HBr and CoH, CH, [63°], (above 360°) Bromo phenanthrene crystallises in thin prisms, v sol HOAc and CS, and is converted by oxidation into phenanthraquinone (Zetter, Hayduck, Anschutz) Bromine (4 mols) acting on phenanthrene in ethereal solution also forms two di-bromo phenanthrenes C14H8Br2 [148°] and [156°] A third di bromo-phenanthrene [202°] is a crystalline powder insol. ether By heating phenanthrene with bromine the compounds C₁₄H₂Br₂ [126°] and C₁₄H₂Br₂ [185°] may be got By heating phenanthrene with bromine and iodine the compounds C₁₄H,Br₆ [245°] and C₁₄H,Br₇ [above 270°] are obtained All these brome-phenomena tallise in needles

(α) - Nitro - phenanthrene C₁₄H₂NO₂. [75°]. Made, together with the two following isomerides, by nitration of phenanthrene (Schmidt, B 12, 1153) Yellow needles Gives (a) nitro phenanthraquinone [215°-220°] on oxidation.

(β) Kitro - phenanthrene. [127°] Less soluble than the (a)-isomeride Yields nitro-phenanthraquinone [260°-266°] on oxidation

(γ) - Nitro - phenanthrene [171°] Small yellow leaflets Less sol alcohol than either of its isomerides Yields on oxidation a nitro-phenanthraquinone [268°]

Di-nitro-phenanthrene C_{1.8}H₄(NO₂)₂. [150°-160°] Made by prolonged action of HNO₂ on phenanthrene (Graebe) Yellow crystals

Bromo-nitro-phenanthrene C.H.(NO₂) CBr [196°] Made by nitration of bromo phenanthrene (Anschütz, B 11, 1218) Long spikes

(a)-Amido-phenanthrene C₁,H₂NH₂ Got by reduction of (a)-nitro phenanthrene (Schmidt, B 12, 1156)
 Small leaflets, insol water — B'HCl crystalline pp —B'₂H₂SO₄ powder

(β) Amido-phenanthrene. Small leaflets — B'HCl sl sol water

(γ)-Amido-phenanthrene Got, like the preceding bodies, by reduction of the corresponding natro phenanthrene—B'HCl glistening needles

Oxy-phenanthrene v PHENANTHROL

Di-oxy-phenanthrene v. Hydro-phenanthraquinone

Pseudophenanthrene C_{1e}H₁₂ [115°] Occurs in crude anthracene (Zeidler, A 191, 295) Large white plates, yielding on oxidation a quinone [170°] which is v sol alcohol and benzene The picric acid compound [147°] separates in bright-red needles on mixing saturated alcoholic solutions of pseudophenanthrene and picric acid

A hydrocarbon $C_{18}H_{10}$ or $C_{14}H_{10}$, [104°], possibly a mixture of phenanthrene with pseudophenanthrene, was got by Zeidler (A 191, 292) from crude anthracene It yields an orange piorate [142°], a quinone [205°–209], insol NaHSO₃ (difference from phenanthraquinone), and a bromide [95°] which changes on fusion to a compound [88°], and on boiling with alcoholic potash forms yellow needles [250°] The quinone gives Laubenheimer's reaction

(a)-PHENANTHRENE CARBOXYLIC ACID CO₂H C₆H, CH [266°] Formed by the action

O₆H₄ CH [200°] Formed by the action of alcoholic potash on the nitrile which is got by distilling sodium phenanthrene (a) sulphonate (2 pts) with K₄FeCy₆ (3 pts) (Japp a Schultz, B 10, 1661, C J 37, 86) Colourless curved blades (from HOAc) or fern shaped leaves (by sublimation), almost insol water Yields phenanthraquinone carboxylic acid on oxidation by CrO₂ and HOAc—NaA'4aq S (of NaA') 68 at 20°—BaA'₂7aq S (of BaA'₂) 066 at 20°, 56 at 100°

Phenanthrene (\$)-carboxylic acid
C.H. C.CO.H. [c 252°] Formed in like manner from a calcium phenanthrene sulphonate contained in the mother-liquid from which its (a)-isomeride has crystallised (Japp) Stellate groups of straight needles (from HOAc), insol water, sol alcohol, ether, and HOAc Yields phenanthraquinone on oxidation—NaA'5aq lamins S (of NaA') 62 at 20°, v e. sol. boiling water—BaA', 6aq rectangular lamins S. (of BaA',) 27 at 20°, 8.7 at 100°.

PHENANTHRENE (a) SULPHONIC ACID SO₂H C₂H₁ CH Made, together with a (β)-acid which forms more soluble salts, by heating phenanthrene (1 pt) with H₂SO₄ (1 pt) at 100° (Graebe, A 167, 152, Japp, C J 87, 93, B 11 213) Crystalline mass, m sol wat r Yields phthalic acid on oxidation—CaA' 4aq small plates, v sol hot water—PbA'₂2aq crystalline

Phenanthrene sulphonic acid C₁₄H_o SO₃H Got by heating phenanthrene (3 pts) with H₂SO₄ (2 pts) at 170° (Morton a Geyer, A C J 2, 203, B 13, 1870) Pearly needles, sol water and alcohol Its salts are less soluble than those of the (a)-acid—KA'—BaA'₂Sr₄—PbA'₂Saq

Phenanthrene disulphonic acid $C_{14}H_{16}(SO_{14}H)_{2}$ Formed by heating phenanthrene with fuming $H_{2}SO_{4}$ (E Fischer, B 13, 314, Hazura a Julius, M 5, 188) Syrup — $K_{2}A''$ xaq powder, v sol water —BaA'' — $Ag_{2}A''$ yellowish powder

Bromo-phenanthrene sulphonic acid $C_{14}B_{15}(SO_{2}H)$ Made by sulphonating bromo phenanthrene (Anschutz a Siemensky, B 13, 1179)—KA' needles, sl sol water— BaA'_{2} in soluble pp—AgA' glistening needles

PHENANTHRIDINE C₁₂H₂N to C₂H₄ CH CH C₃H₄ N VD 65 [104°] (360°) Made by passing the vapour of benzylidene-aniline through a red hot tube (Pictet a Ankersmit, B 22, 3339) White needles, v e sol alcohol, sl sol hot water Its aqueous solution shows blue fluorescence NaNO, gives a bulky pp of the nitrite Tin and HCl give a hydride crystallising in needles [100°]—B'HCl needles, v sol water—B'H2PtCl₄ needles—B'HAuCl₄—B'HHgCl₃ [190°]—B'C₆H₄N₄O, needles—B'H₂Cr₂O,

Methylo-rodide B'MeI [201°]

Oxy phenanthridine $\overset{\bullet}{C_0H_4}\overset{\bullet}{NH}$ Got by reducing o-nitro-o phenyl benzoic acid with zinc dust and ammonia. It yields phenanthridine on distillation with zinc dust

PHENANTHROL C₁₁H₂ OH [112°] Formed by potash fusion from phenanthrene sulphonic acid (Rehs, B 10, 1253) Thin lamine (from benzene ligroin), with bluish fluorescence V sol alcohol and ether, sl sol water, v sol alkalis

Acetyl derivative C14H, OAc [118°]

PHENANTHROLINE C₁₂H₈N₂ t c
CH CH C CH CH C N CH
[78°] (above 860°)
Prepared by heating m phenylene diamine or
(B 3) amido quinoline with nitro benzene,
glycerin, and H₂SO₄ (Skraup, B 15, 895, M 3,
578, 5, 532, La Coste, B 16, 674) Got also
by heating its carboxylio and [209°] (Gerdeissen,
B 22, 252) Colourless anhydrous four-sided
tables [78°] or needles (containing aq) [66°] M
sol hot water, v sol alcohol, v sl sol ether
Fromine gives in a solution of its hydrochloride
a crystalline pp C₁₂H₂N₂Br₂ [149°], converted
by hot alcohol into C₂₄H₁N₂Br₂ [178°] KMnO₄
crystals it to durity and

oxidises it to dipyridyl dicarboxylic acid
Salts —B"H_Cl_2aq colourless prisms Its
aqueous solution yields on evaporation lon
prisms of B'HClaq —B'HBr 3aq [280°] B'H_Cr_O,: goldenneedles.—B'O,H_N,O,. [288°].
—B'H_PtOl_aq —B'HNO, prisms, m sol hot

water

Methylo-iodide B'MeI 2aq Golden prisms, sol water, sl sol alcohol, insol ether

Oxy-phenanthroline [160°]. C,2H8N2O Formed in small quantity, together with phenanthroline, by heating m nitro aniline with lycerin, eitro-benzene, and H₂SO, (La Coste) Needles (fr m benzene) —B'2H2PtCl aq

Methyl-phenanthroline v p 855

D1-methyl-phenanthroline CH CH C CH CH C N CMe CMe N C CH CH [98°] Formed by the action of paraldehyde and HClAq at 100° on m phenylene-diamine or (B 3) amido (Py 3)methyl grapoline (Von Miller a Niederlander, B 24, 1740, Scruff, B 24, 2127) Colourless Melts at 78° when conneedles (from water) taining water of crystallisation V sol alcohol, volatile with steam Yields on reduction a base BzCl forms O14H19BzN2 [164°].

B'2H2PtCla Di hexyl di amyl-phenanthroline C₅H₁₁ C CH C CH OH C N C C₆H₁₅ C₆H₁₅ C N C CH C C C₅H₁₁ Formed by the action of conanthol on an alcoholic solution of m phenylene diamine or of amido-hexyl-amyl quinoline at 100° (Von Miller a Gerdeissen, B 24, 1731, cf Schiff, A 253, 322) Needles Its alcohol solution does not

522) Needles Its alcohol solution does not fluoresco —B'HCl —B'H_PtCl, 2aq [201°-210°] Orange powder —B'C,H,N,O, [104°] Needles Pseudo phenanthroline Cl, H,N, 1 te CH CH CH CH CH CH (173°) Made from CH CH CH CH — C CH CH p phenylene diamine, glycerin, H2SO, and nitro benzene (Skraup a Vortmann, M 4, 569), and from Ph N₂ C₆H₄NH₂, glycerin, and H₂SO₄ (Lellmann a Lippert, B 24, 2623) Obtained also as a by-product in the preparation of (B 3)-nitroquinoline from p nitro aniline (Bornemann, B 19, 2377) Crystallises from water in needles (containing 4aq), v sol alcohol, sl sol ether Oxidised by KMnO, to dipyridyl dicarboxylic acid

Salts — B"HCl 2aq plates — B"H₂Cl₂ monoclinic prisms — B"H₂PtCl₂ 2½aq — B"H₂Br₂. - B"H,Br, - B"Br, - B"I, - B"HI, - B"H

Methylo vodedes B"Mel aq lemon yellow needles — B"Me, I, aq red tables PHENANTHROLINE (B) CARBOXYLIC

PHENANTHROLINE (B) CARBOXYLIC ACID C₁₂H₂(CO₂H)N₂ [277°] Formed by oxidation of (B) methyl phenanthroline with chromic scid (Skraup a Fischer, M 5,527) Minute needles, sl sol water and alcohol, sol alkalis and acids — Ca,HA', 10aq needles Yields phenanthroline on distillation with alkalis

Phenanthroline (Py 3)-carboxylic acid $O_{12}H_7(CO_2H)N_2[N\ CO_2H=1\ 2]$ [209°] For Formed by oxidation of (a)-methyl phenanthroline with KMnO, and H₂SO₄ (Gerdeissen, B 22, 250) Pale-yellow needles (containing aq), v sl. sol. cold water

Phenanthrone v PHENANTHRAQUINONE PHENANTHROXYLENE - ACETOACETIC ACID Ethyl ether C₂₀H₁₆O₄ s.e. C₂H₄ O CAc CO₂Et Mol w (by Racult Mol w (by Raoult's method) O.H. CO

287 (calc. 820) [185°] Formed by heating phenanthraquinone with acetoacetic ether and NE Aq or KOHAq (Japp a Streatfeild, O J 48, 27, Japp a. Klingemann, C J 59, 2) White silky needles, v. sol. hot benzene and alcohol.

Reactions — 1. Alcoholic potash forms $C_1, H_{12}O_2$ crystallising from alcohol, after solution at 100° in sealed tubes, in needles [259°] — 2 Alcoholic ammona at 100° yields lustrous yellowlamins [168°] of $C_{40}H_{28}$ or $_{40}N_{4}O_{5}$ — 3 Alcoholic HCl yields $C_{20}H_{15}$ ClO₃ [146°], whence alcoholic NH₂ produces $C_{40}H_{21}NO_{6}$ — 4 Heating with NH₂ produces $C_{ia}H_{a_1}NO_a - 4$ Heating with HOAc forms three compounds, $C_{ib}H_{1i}O_3$, decomposing at 285° without melting, $C_{ib}H_{1i}AcO_4$ [165°-171°], and $C_{4i}H_{2i}O_3$ [227°] -5 Propionic acid at 140° yields silky needles $C_{2a}H_{1i}O_3$ and crystalline $C_{2a}H_{2a}O_3$, which body is also got by heating with propionic anhydride at 150° -6 HI and P yield $C_{2a}H_{1i}O_3$ [128°], whence potash forms an acid $C_{1a}H_{1i}O_4$ [295°], which gives BaA" 2aq and Ag₂A" -7 Heated on the water bath with alcohol contaminate few drops of H. SO, it forms alcohol containing a few drops of H₂SO₄, it forms C₁,H₁₀O(OEt)(CO₂Et) [144°], which yields, with phenyl - hydrazine, C₁,H₁₀(N₂HPh)(OEt)(CO₂Et) [220°] and, on hydrolysis, C₁₆H₁₁(OEt)(CO₂H)₂ [203°], crystallising in colourless needles -8 Alcohol containing a large quantity of H₂SO₄ forms C₂₂H₂₀O₄ [144°], sol boiling alcohol, and C₁,H₁₂O₂ [277°], insol alcohol

Isophenenthroxylene acetoacetic acid

C₁₈H₁₂O₄ [269°] Formed by saponifying its ether with NaOH (Japp a Klingemann, C J 59, 14) Flat needles (from alcohol) Conc KOHAq at 150° yields C₁₁H₁₀O Ac₂O at 150° forms C₁₇H₁₀O, insol. alcohol, and C₁₉H_{14 oz 16}O, [226°] —CuA', 9aq

Ethyl ether EtA' [177°] Formed from phenanthroxylene acetoacetic ether by heating with formic acid (S G 1 22) at 130° for an hour, or by boiling with H2SO, diluted with twice its weight of water (Japp a Klingemann, C J 59, Colourless triclinic prisms (from EtOAc), c = 9641507, $\alpha = 78^{\circ} 6'$, $\beta = 72^{\circ} 0'$, abc = 9641507, $\gamma = 83^{\circ}$ 18', sol alcohol, benzene, and light

petroleum

Reactions -1 Ac₂O at 150° forms the acetyl derivative C₂₀H₁₈AcO₄ [165°-170°], crystallising from benzene in needles -2 Phenyl hydrazme in alcoholic solution at 135° yields the compound C₂₀H₁₆(N₂HPh)O₃ crystallising in yellow needles [212°] —8 Zinc and HCl yield a crystalline compound [165°-170°], and also C₂₀H₁₆O₃ [125°], a body which yields a phenyl hydrazide a body which yields a phenyi hydrazude $C_{20}H_{14}(N_1HPh)O_2-4$ Bromine in CHCl, yields $C_{20}H_{13}BrO_4$ [212°] crystallising in yellow prisms and tables -5 HIAq at 100° forms $C_{11}H_{12}O$ [215°] crystallising in slender flat needles

PHENAZINE C12H5N2 to CH4 NOCH4 Asophenylene [171°] (above 360°) S (alcohol) 2 in the cold

Formation -1 By distilling m- or p azobenzoic acid with excess of lime (Claus, B 5, 367, 610, 6, 723, 8, 39, 600, 10, 1303, A 168, 1) -2 By passing aniline over red-hot PbO (Schichutzky, J R 6, 248), or merely through a red-hot tube (Bernthsen, B 19, 8256) -3 By heating equal weights of pyrocatechin and o-phenylene diamine at 205°, followed by atmo-spheric exidation of the resulting dihydride (Ris, B 19, 2206)—4 By heating o-amidophenol and oxidising in the same way (Ris) -5 From di-amido phenazine by the diazo- reaction (O Fischer a Hepp, B 22, 358; Nietaki, B 28, 1855)

Properties -Long yellowish needles (by sub-

limation), v sol hot alcohol and ether, v sl sol. hot water H2SO4 forms a blood red solution, becoming yellow on dilution Volatile with steam Combines with bromine, forming C12H8N2Br2, which separates from benzene in yellow needles, and with chlorine, forming C12H8N2Cl2 as unstable

red crystals (from alcohol)

Salts -B'HOL Tables (from HClAq), decomposed by hot water — B'HAuCl, crystals — B'HHgCl, —B',HPtCl, 22q yellow plates—B'HI Dark-green needles—B'HBr Brown crystals—B'O, H,N,O, [180°-190°] Long yellow needles, sol cold alcohol—B'Hg(No), Brown Long yelruby-red crystals (from HNO₂) -B'2AgNO₂

Dihydride C12H10N2 is C.H4 NH C.H. Formed by reduction of phenazine with alcoholic NH, and H₂S (Claus, A 168, 8) Trimetric lamine, almost insol water and benzene, v sl sol cold alcohol Conc H2SO4 forms a green solution, turning red on further addition of H.80, and green on cautious addition of water, in this reaction an unstable base C24H18N4 appears to be formed, giving the salts B"H₂Cl₂ and B"H₂PtCl₅, the latter forming in green needles

Di-chloro phenazine C12HaCl2N2 Made from phenazine and POl

Nitro-phenazine C₁₂H₇(NO₂)N₂ [210°] Made by nitration Yellowish green needles

Amido-phenazine $C_6H_4 < N > C_6H_3(NH_2)\begin{bmatrix} 1 \\ 2 \end{bmatrix}$ [265°] Got by sublimation from a mixture of di amido phenazine and zinc dust (O Fischer a Hepp, B 22, 357) Long red needles with bronze lustre (from alcohol) Strong base Its dilute solution shows orange red fluorescence -B',H,PtCl, 21aq

u-Di-amido phenazine C12H10N4 te

C.H. NCCHCNH A product of oxidation of ophenylene-diamine by FeCl₂ (Fischer a Hepp, B 22, 355, 23, 841, 2788, cf Griess, B 5, 202, Rudolph, B 12, 2211, Wiesinger, A 224, 353) Formed also from ophenylene discontinuous and the statement of the st amine and CyI (cf Hubner, B 9, 777, 10, 1715), and by boiling o phenylene diamine hydro-chloride (25g) with amido-azo benzene (3g) and acetic acid (80 g of 75 pc) for two hours Long brownish-yellow needles or yellow plates (by sublimation) Conc H2SO4 forms a grassgreen solution, turned red on dilution Its solution in benzene or alcohol fluoresces greenishyellow Alcoholic solutions of the salts fluoresce dark orange red Yields with benzil the quinoxaline C₂₆H₁₆N₄ - B'HCl 3aq -B'₂H₂SO₄ 3aq Dr-acetyl derivative C12H.Ac2N.

270°] Yellow needles Di-formyl derivative Reddish-yellow mass

s-Di-amido-phenasıne

 $\begin{bmatrix} 1 & 3 \\ 4 \end{bmatrix} & O_0H_1(NH_2) < N > C_0H_3NH_2 & 1 \end{bmatrix} [280^\circ]$ Got by heating the tin double salt of tri amidodiphenylamine with water, CaCO, and MnO, (Nietzki, B 28, 1854) Long dark yellow needles, v e sol alcohol, ether, and hot water Yields phenazine on elimination of amidogen -B"HNO, greenish needles.—B"C,H,N,O,

Dr-active derivative C1. H1. N.O.

Tri amido-phenazine C12H11Ns i.e. $\begin{bmatrix} 4 & 1 \\ 2 & \end{bmatrix} C_6 H_2 (NH_2) \langle N \rangle C_6 H_2 (NH_2)_2 \begin{bmatrix} 1 & 8 \\ 2 & 4 \text{ or } 6 \end{bmatrix}$ Made by passing a current of oxygen through a solution of a triamidobenzene hydrochloride (10 g) and NaOAc (18 g) (E Muller, B 22, 856, cf Witt, B 10, 658) Brown needler m sol hot of Witt, B 10, 658) Brown needler m sol hot alcohol and water, the solutions showing yellow fluorescence Cone H2SO4 gives a yellow solu tion, changing violet, red, and finally yellow on dilution It decomposes when heated to 100° -B"(HNO₃)₂ 2aq needles with green lustre Forms a crimson solution with yellow fluores cence The solution becomes yellor (a dilution Tri-acetyl derivative JigH.Ac.N.

Tetra-amido-phenazine

NH₂ C CH C N C CH C NH₂ Formed by passing NH₂ C CH C N C CH C NH₂ air through a hot solution of tetra amido benz ene hydrochloride (10 g) and NaOAc (20 g) (Nietzki a E Müller, B 22, 447) Brown needles (from hot water or alcohol), or yellow needles containing aniline of crystallisation (from aniline) Its solutions exhibit yellowish green fluorescence Conc H₂SO, forms a yellow solu tion, passing, on dilution, through blue, violet, and red, to yellow -B"(HNO₃)₂ 2aq lustrous green needles giving a crimson solution

References -METHYL-PHENAZINE and DI-OXY

PHENAZINE

Tolylene red $C_eH_s(NMe_2) < N > C_eH_2Me(NH_2)$ is also a phenazine derivative (Bernthsen, A 236, 332)

PHENTRIAZINE (235°-240°) Formed from the formyl derivative of o nitro phenyl hydrazine, alcohol, HOAc, and sodium amalgam (Bischler, B 22, 2806), and by the action of P_2O_5 on o amido phenyl methyl hydrazine (Hempel, J pr [2] 41, 174) Yellow needles, v sol warm water and cold alcohol, very volatile with steam

TRIPHENAZINE DIHYDRIDE

 $C_eH_4 < NH > C_eH_2 < NH > C_eH_4$ dine Formed by heating u di amido phenazine hydrochloride (4 pts) with o phenylene diamine at 205° for 15 minutes (Fischer a Hepp, B 23, 2791) Bluish violet powder or lustrous green needles, v sl sol alcohol, forming a violet red solution with vellowish red fluorescence Solutions of its salts are blue, with brownish red fluorescence

PHENAZOKINE C,H, NH C,H, or oxido-diphenyl amine [148°] Obtained by heating together equal quantities of o-amido-phenol and pyrocatechin at 260°-280° Silvery scales. V sol alcohol, ether, chloroform, and benzene Sublimable Distils, in great part undecomposed By nitration and reduction the leuco-base of a violet dye stuff is obtained (Bernthsen, B 20, 942)

PHENBUTYL- COMPOUNDS BUTTE PRENTL- COMPOUNDS

PHENISOBUTYL CYANIDE v. Iso-BUTYL BENZONITRILE.

PHENISORUTYL - PHENETHYL - THIO UREA v. ETHYL PHENYL ISOBUTYL PHENYL THIO-

PHENCAPRYLAMINE & AMIDO-PHENYLOCTANE

PHENENYL TRIBENZOIC ACID C₂,H₁₈O₆ [261°] G at by potash fusion from tri-benzovl ene benzene (Gabriel a Michael, B. 11, 1008) Prisms, v soi alcohol, ether, and HOAc Yields C₆H₂Ph₃ when distilled with lime—Na₃A'"—Ag₃A'"—Ag₃A''

PHENENYL TRI-METHYL TRIKETONE C₈H_{*}(CO CH₂), [163°] Formed by the spontaneous condensation of acetoacetic aldehyde (Classen a Stylo* B 21, 1144) Small needles, v sol HOAc, sl sol alcohol, ether, and water Oxidised by nitric acid to trimesic acid

PHENĚTHYLAMINE v Amido-Phenyl-

PHENETHYL - PHENISOBUTYL - THIO - UREA v p ETHYL PHENYL-p ISOBUTYL PHENYL THIO UREA

PHENETIDINE v Ethyl derivative of Amido-

PHENETOL v Ethyl ether of Phenol
DIPHENIC ACID v DIPHENYL DICARBOXYLIC

PHENNAPHTHAZINE C16H16N2 4.6

C₁₀H₆ N C₅H₄ (a3) Naphthophenazine [142°]

Formation —1 By mixing equal mols of o-phenylene diamine and (β) naphthoquinone in 50 p c acetic acid —2 By oxidation of equal mols of o phenylene diamine and (β) naphthol with alkaline potassium ferricyanide —3 By the decomposition of sulpho benzene azo (β) -naphthyl phenyl amine by treatment with boiling dilute mineral acids $C_0H_4(SO_3H)N_2C_0H_6NIC_H_5 = C_{10}H_6N_2C_6H_4 + C_0H_4(NH_2)SO_2H$

Preparation —Fifty grms of the dyestuff are dissolved in 500 cc of boiling water, and 125 cc of conc H₂SO₄ is slowly added to the hot solution, the colour acid, which is first precipitated, re dissolves, and on cooling the sulphate of the azine crystallises out in red needles, whilst

sulphanilic acid remains in solution

Properties—Glistening yellow needles or prisms Sublimes at about 200° in long flat needles Distils undecomposed above 360° Sl sol alcohol, ether, and cold benzene, v sol hot benzene Dissolves in cone H₂SO₄ with a brownish red colour, becoming yellow on di lution

Salts —With each and it forms two different salts —B'HCl* long reddish yellow needles and warty orystals — $B^{\prime}_{.}H_{.}SO_{.}^{\times}$ red needles and thick garnet-red prisms —B'HNO₃* yellow and red needles, both sparingly soluble (Witt, B 20, 579).

PHENOCYANIN C.H., NO or C.H., NO. Dark blue mass with coppery lustre, got by atmospheric oxidation of a mixture of phenol and NH. (Phipson, B 6, 828) Insol water, sol alcohol Coloured red by acids

H F 47,841 (Stohmann, J pr [2] 33,471; 28,000 (Von Rechenberg) Occurs in castoreum (Wöhler, A 67, 360), and in small quantities in urine of cows, horses, and men (Stadeler, A 77, 18, Lieben, A Suppl 7, 240, Hoppe Seyler, C J. 25, 628, Munk, B 9, 1596, Salkowski, B 9, 1596, Baumann, B 9, 54, 1389, 1715) Contained in considerable quantity in coal tar (Runge, P 31, 69, 32, 308, Laurent, A Ch [3] 3, 195), and in the products of the dry distillation of gum benzoin, quinte acid, wood, and bones

Formation -1 By distilling o-, m- or p-, oxy-benzoic acid alone or with lime (Gerhart, Rev scient 10, 210, Rosenthal, Z [2] 5, 627) 2 A product of the distillation of glycerin with CaCl₂ (Linnemann a Zotte, A 174, 87, Suppl 8, 254) -3 By heating anisole with conc HIAq or HClAq at 140° (Graebe, A 139, 149) -4 From aniline by the diazo reaction (Griess, A 137, 39) -5 From benzene sulphonic acid by potash-fusion (Wurtz, Bl [2] 8, 197, cf Degener, J pr [2] 17, 394) -6 From phenol p sulphonic acid by distillation with dilute H₂SO₄ and superheated steam at temperatures above 116° (Armstrong a Miller, C J 45, 148) -7 By heating acetylene with fuming H2SO, and fusing the product with potash (Berthelot, C R 68,539) —8 By shaking benzene with palladium that has absorbed hydrogen and air (Hoppe Seyler, B 12, 1552) -9 By the direct action of hydrogen peroxide on benzene (Leeds, B 14, 975) -10 In small quantity by the action of dry oxygen on boiling benzene containing AlCl, (Friedel a Crafts, A Ch [6] 14, 435, C R 86, 884) —11 A product of fermentation of proteids (Baumann, B 10, 685, Weyl, H 1, 339, Brieger, J pr [2] 17, 134

Preparation—The aqueous solution got by stirring coal tar oil with NaOHAq is diluted with water as long as naphthalene separates. The liquid is then exposed to the air, with frequent stirring, for several days, and then fractionally ppd by acid (e.g. CO.), the last fraction being nearly pure phenol. The phenol is dried by heating to boiling in a current of air, and further purified by crystallisation (Hugo Miller, Z. [2] 1, 270, cf Williamson a Scrugham, C. J. 7, 232). Phenol may also be dried by distilling over dried CuSO. (Bickerdike, C. N. 16, 188, cf.

Gladstone, C N 2, 98)

Properties - Long deliquescent needles. with strong smell, m sol water, miscible with alcohol and ether Attacks the skin Does not redden litmus Nearly insol Na, CO, Aq, m. sol. NH, Aq, v sol KOHAq and NaOHAq Antiseptic Not affected by distillation with P,O,, lime, or BaO A solution of phenol even in 43,000 pts of water gives a pp of tri-bromophenol on addition of bromine-water (Landolt, B 4, 770) FeCl, gives a violet colour to an aqueous solution, the reaction is prevented by acetic acid and by alcohol (Hesse, A 182, 161) Cone H2SO, poured beneath a solution containing phenol and nitric acid (1 pc) gives an intense red ring, with nitrous acid, red and green rings are got, with chlorates, a pale-yellow ring with blue below (Lindo, C N 58, 1, 15) An aqueous solution of phenol (4 vols) mixed with ammonia (1 vol) myes on warming with a few drops of bleaching powder solution a blue colour

which becomes red on addition of soids (Salkow-ski, Fr 11, 316) Boiling aqueous mercurous intrate gives a deep-red colour (Plugge, Fr 11, 178) Millon's reagent gives on boiling a yellow pp which dissolves in nitric soid forming a deep red liquid, salicylic soid behaves in like manner (Almén, J 1878, 1079) On adding p-oxybenzoic aldehyde and an equal volume of H₂SO₄ a yellow liquid is got, turned crimson by potash (aurin) Phenol is poisonous (Wöhler, A 65, 844. Dunlay a Garin, C R 112, 627)

344, Duplay a Carin, C R 112, 627) Reactions - 1 Decomposed by passing through a red-hot tube yielding benzene, toluene, xylene, naphthalene, anthracene, and phenanthrene (Kramers, A 189,129) When crude phenol is used the product deposits a crystalline hydrocarbon C₁₀H₁₂ [32 9°], S G 178 1 012 (63° at 9 mm) This hydrocarbon is volatile in the cold, smells like camphor, and is sol alcohol, ether, and petroleum-spirit It is resimified by atmospheric oxygen It absorbs bromine, yielding a liquid bromide By heating for 4 hours at 100° in vacuo the hydrocarbon is polymerised, yield ing a solid [200°-220°] (Roscoe, C J 47,669) -2 Chlorene forms o- and p-chloro phenol (4,2,1)-di-chloro-phenol, (6,4,2,1) tri-chloro phenol, and tetra-, pent-, and hexa-chloro-phenols Exhaustive chlorination gives CaCla, COla, CaCla, and COa (Ruoff, B 9, 1483) An intermediate body is $C_{12}Cl_2O_2$ [823°] (Hugounenq, C R 109, 309) KClO, and HCl yield tri-chloro-phenol and triand tetra- chloro-quinone -3 Chlorine acting on phenol in alkaline solution forms the acid C(OH) CCl₂ C(OH) CO₂H (Hantzsch, B) 2780, 22, 1238) — 4 Bromne-water forms tribromo-phenol Heat (68492 units) is given out in the reaction Br in excess gives C.H.Br.O (Werner, C R 100, 799, Bl [2] 46, 280) —5 *Iodine* and alkali at 60° form $C_0H_3I_3O$ [157°], which is violet red, insol water, and forms a red solution in alcohol and ether It is converted into tri iodo-phenol by boiling with KOHAq (Messinger a. Vortmann, B 22, 2313) — 6 Chloride of vodine forms mono- and di-, iodo-phenol (Schützenberger, C R 54, 197)—7 Oxidised by intro bensene and dilute NaOH in the cold to oxalic acid and CO, (Siegfried, J pr [2] 31, 542) -8 If a rapidly alternating electric current be passed through a solution containing phenol, magnesic sulphate, and magnesic bicar bonate, the following bodies are formed, owing to the rapidly alternating oxidation and reduc tion: pyrocatechin, hydroquinone, di oxy diphenyl, formic acid, succinic acid, and oxalic acid (E Drechsel, J pr [2] 29, 249) Another product is C₆H₁₀O, an oil (158°-178°) with aromatic smell which forms a phenyl hydrazide C12H12N [108°] By continuing the alternating current this oil is converted in n hexoic acid -9 Electrolysis with carbon electrodes in aqueous solution rendered slightly alkaline by KOH yields a di-oxy-benzoic acid C,H,O, [98°] and an amorphous acid C₆₅H₄₈O₅₂ insol water and ether, sol alcohol The amorphous acid yields piorio acid with HNO3, and on protracted boiling with dilute HClAq it yields amorphous infusible $C_{\rm ti}H_{\rm se}O_{\rm ls}$ and amorphous $C_{\rm n}H_{\rm se}O_{\rm s}$ [60°], sol water, alcohol, and ether In like manner NaOPh yields on electrolysis C₂₉H₂₀O₃ separahle by hot HClAq into mfusible C, H, O, msol. water and ether, and

 $C_{12}H_{10}O_{3}$ [78°], sol water (Bartoli a Papasogli, G14,90) -10 Taken internally it is partly oxidised to hydroquinone and pyrocatechin (Nencki a Giacoso, H 4, 325) —11 H_2O_2 oxidises it to pyrocatechin, hydroquinone, and quinone (Martinon, cateonin, nyaroquinone, and quinone (maximum, Bl [2] 48, 156) When treated in aqueous solution with NH₃, H₂O₂, Na₂OO₃, and hydrox, lamine hydrochloride it yields r ienolquinon-mide, which colours the liquic bright blue (Wurster, B 20, 2934) —12 CrO₂Ol₃, followed by water, gives O(C,H,OH)2 (Etard) CrO2Cl2 and HOAc give tri- and tetra- chloro-quinone (Carstenjen, J pr [2] 2, 82) -18 Fusion with NaOH yields resoroin, pyrocatechin, and phloroglucin Potash fusion gives o and m-oxy-benzoic acids and two di oxy diphenyls (Borth a Schreder, B 11, 1332, 12, 417) -14 PCla forms PCl2(OPh), PCl(OPh)2, and P(OPh)3, which may be separated by fractional distillation we vacuo (Noack, A 218, 85, Anschutz a Emery, A 239, 310, A 253, 110) The compound PCl₄(OPh), (90° at 11 mm), (216° at 760), S G 20 1 354, is converted by chlorine into PCl4(OPh), whence SO₂ produces POCl₂(OPh) (122° at 11 mm) Bromine converts PCl₂(OPh) into PCl2Br2(OPh), which is crystalline but very un-Sulphur at 190° converts PCL (OPh) into PSCI₂(OPh), a colourless liquid (120° at 11 mm), SG ²⁰ 14059 The compound PCI(OPh)₂ (172° at 11 mm) (295° at 760 mm) is converted by chlorine into PCl, (OPh), which is crystalline, and insol other Bromine converts PCl(OPh), in ether into orange yellow crystals of PCIBr₄(OPh). Sulphur and PCI(OPh)₂ at 190° yield PSCI(OPh)₃, crystallising in colourless needles [64°], (194° at 11 mm) Tri-phenyl phosphite P(OPh)₄ combines with chlorine, formng PCl₂(OPh)₃, whence water produces triphenyl-phosphate PO(OPh)₃ [45°] (245° at 11 mm) P(OPh)₃ with sulphur at 190° yields PS(OPh)₃ [50°] (245° at 11 mm) S G ³⁰ 1 2341 -15 PCl, forms hardly any chloro-benzene (Otto, A 145, 817, cf Glutz, A 143, 181) -16 P_2S_2 forms, on heating, phenyl mercaptan, diphenylenedisulphide $O_{12}H_8S_2$, and some Ph_2S (Kekulé, C. R 64, 752, Graebe, B 7, 51, 397, Geuther, A. 221, 57) P_2S_3 forms benzene, Ph.PO4, and H.S -17 Aqueous KMnO4 oxidises Ph₂PO₄, and H₂S —17 Aqueous KMnO₄ oxidises it to oxalic acid and CO₂ (Tollens, Z [2] 4, 715) —18 Distillation over heated zinc dust yields benzene—19 H₂SO₄ (1 pt) forms o and p sulphonic acids (Kekulé, Z [2] 3, 197) H₂SO₄ (1½ pts) at 160° forms di oxy di phenyi sulphone (Glutz, A 147, 52) K₂S₂O₅, heated with a solution of KOC₂H₃ at 65°—70°, forms C₂H₄O SO₂OK, which crystallises in tables, S 14 at 15°, soil hot alcohol This salt occurs in urine It is decomposed by boiling with water and dilute acids into phenol and H₂SO. At 150° the dry salt changes to the isomeric potassium phenol p-sulphonate Phenyl sulphuric acid is also a product of the passage of a rapidly-alternating electric current through a solution of phenol, MgSO4, and magnesium bicarbonate acid is very unstable (Baumann, B 11, 1907; Brieger, H 8, 311, Drechsel, J pr [2] 29, 240) — 20 SO, Cl. at 150° forms chloro-phenol (Dubois, Z [2] 2, 705) S₂O₃Cl₂ forms o anu p chlorophenols and their sulphonic acids (Armstrong a. Pike, C N 29, 288) -21 Nitric and forms o and p- nitro-, di-nitro, and tri-nitro- phenola-

22 Potassium and sodium dissolve, giving off hydrogen and forming phenylates These absorb CO₂, forming PhO CO₂K and PhO CO₂Na, which yield oxy-benzoates when strongly heated (v O OXY BENZOIC ACID) (Kolbe, J pr [2] 10, 89) — 23 CrO, forms phenoquinone C₁₈H₁₄O₄ (Wichelhaus, B 5, 248, 846)—24 Netrous and forms nitroso phetol, the mono-oxim of quinone (Baeyer, B 7, 967) H₂SO₄, to which 6 pc of KNO2 has been added, gives when shaken with a mixture of phenol (1 vol) and H₂SO, (1 vol) a brown colour, changing to green, and finally to a magnificent blue On pouring into water brown flakes are deposited (Liebermann, B 7, 248 1098) In the action of H₂SO, and nitrous acid on phenol there is formed (a)-phenol di-chroin $C_{18}H_{18}NO_{2}$ or $C_{6}H_{4}(OH)N(OPh)_{2}$?, a brown powder, sol ether, and also phenoloxy chroin $C_{18}H_{18}NO_4$, which is black and insole ther (Kramer, B 17, 1877, Brunner a Chuit, B 21, 250) (a) Phenol dichroïn is also formed from quinone mono oxim and H2SO4 (Baeyer a Caro, B 7,966) Each body yields an amorphous acetyl derivative Phenol-dichroin forms a blue solution in alkalis and H₂SO₄ Phenol oxychroïn forms a green solution in H₂SO₄, and a brown solution in alkalis -25 NOCl gives chlorinated quinones (Tilden, C J 27, 851) —26 Distillation with PbO yields diphenylene oxide $C_{12}H_{2}O$ and C₁₃H₈O₂, crystallising in needles [174°] (Graebe, B 7, 396, Behr a Van Dorp, B 7, 398) -27 COCl₂ at 150° forms CO(OPh)₂ and COCl(OPh) (Kempf, J pr [2] 1, 402) -28 Ammoniacalezine chloride at 290° forms aniline, diphenylamine, and Ph₂O(Merza Weith, B 13,1299) 29 Hydrazin, solution in excess forms a white unstable substance [57°], possibly $C_6H_6O(N_2H_4)$ (Curtus a Thun, J pr [2] 44, 190) —30 TiCl₄ acting on a benzene solution of phenol forms dark red crystals of Ti(OPh), HCl, decomposed by water into phenol, titanic acid, and HCl (Schumann, B 21, 1079) —31 AlCl, gives the solid Al₂Cl₂(OPh), v sol hot CS₂, insol ligroin, decomposed at once by water into phenol, alu mina, and HCl (Claus a Merklin, B 18, 2933) On heating phenol (2 pts) with AlCl, (1 pt), benzene, Ph₂O, and diphenylene methane oxide are formed (Merz a Weith, B 14, 191) Phenol (5 g) added to AlBr_s (10 g) forms amorphous Al₂Br₃(OPh)₃, which is quickly decomposed by water (Gustavson, J R 16, 242) —32 AlCl₃ and CCl₃NO, followed by water give aurin —33 Heating with exalic acid and H₂SO, gives resolic acid 34 Cyanic acid vapour is absorbed by dry phenol forming phenyl allophanate, which crys tallises from hot alcohol in unctuous crystals (Tuttle, J 1857, 451) —35 Bensyl chlorude and zinc form PhOH, C. H.OH on heating (Paterno, G. 2, 2) —36 Phenol (10g) boiled with Ac.O (20 g) and ZnCl₂ (20 g) forms phenacetein, a red dye C₁₆H₁₂O₂, which is insol benzene, sol alcohol, ether, and HOAc Its solution in alkalis 18 raspberry-red (Rasiński, J pr [2] 26, 54) — 87 C₆H₄ CCl, forms benzaurin —38 Phthalic anhydride and H₂SO₄ form phenol phthalein C₂₂H₁₄O₄ on heating (Baeyer, B 4, 658) — 89—Acetamide and benzamide on heating form respectively PhOAc and PhOBz, while NH, is given off (Guareschi, A 171, 140) -40 Heated in a doholic solution with CCl, and KOH or NaOH it yields o- and p- oxy benzoic soids -Vor. III

41 Paraldehyde and stannic chloride form CH₂ CH(C₂H₄OH)₂ -42 Bensoic aldehyde, alcohol, and a few drops of HCl form white resinous C₂₆H₂₀O₂, whence amorphous C₂₆H₁₈Ac₂O₂ may be got (Michael a Ryder, Am 9, 130) — 43 Bensene sulphochloride added to a slightly alkaline solution of phenol forms C.H.SO. OPh as very stable colourless crystals [36°], sol alcohol, sl sol ether, saponified by alcoholic potash (Georgesen, B 24, 417) -44 Acetoacetic ether and H.SO, form (\$) methyl coumarin — 45 Chloro-acetal and alcoholic NaOPh at 160° form C₂H₃ O CH₂ CH(OEt)₂ (255°) (Autenrieth, B 24, 162) -46 CCl₃ COCl and AlCl₃ give discount of the color of phenyl carbonate (Heutschel, J pr [2], 36, 315) 47 o Oxy-benzoic aldehyde, HOAc, and H.SO. form, on warming, oxyaurin C19H14O4, which greatly resembles aurin (Liebermann, B 9, 801, 11, 1436) Zulkowsky (M 5, 111) obtained a dyestuff C₂₆H₂₀O₄ soluble in aqueous NaHSO₃, and another dyestuff insol NaHSO, Aq -48 CH, CCl, and dilute caustic soda form CH, C(OPh), [98 5°] crystallising in plates, v sl sol water (Heiber, B 24, 3678)

Estimation -1 Titrated by adding bromine water till the solution is yellow, or by adding excess of bromine, KI, and starch, then titrating with Na2S2O2 The bromine solution contains 40 grms Br and 20 grms KBr per litre (Degener, J pr [2] 17, 380, cf Landolt, B 4, 770, Koppeschaar, Fr 15, 233, Weinreb a Bondi, M 6, 506, Giacosa, H 6, 45) -2 14 to 15 grms of pure KOH are dissolved in 1 litre of water and 10 grms of bromine gradually added, the solution is then diluted till 50 cc corresponds to 005 grm of pure phenol To ascertain the strength of any phenol solution 50 grms of the above solution are taken and the phenol added till a drop of the solution ceases to give a blue colouration with KI and starch (Chandelon, Bl [2] 38, 69) -3 2 or 3 grms phenol are dissolved in three times the molecular proportion of caustic soda The solution is made up to 500 cc, and 10 cc are put into a small flask warmed to 60°, and one tenth normal iodine solution is allowed to flow in until it is coloured strongly yellow by excess of iodine, by shaking, a red pp is formed The excess of iodine is estimated by sodium thio sulphate The excess of The quantity of iodine taken up by the phenol multiplied by 0 123518 gives the amount of pure phenol (Messinger a Vortmann, B 23, 2753) -4 To separate phenol from mixtures in poisoning cases the substance is triturated with dilute H2SO, and extracted with alcohol, the alcohol evaporated, and the residue extracted with benzene (Dragendorff a Jacobson, C C 1886, 828), or the alcoholic extract may be mixed with NaOHAq, evaporated to a small bulk, filtered, and the phenol ppd by HClAq in a graduated tube (Muter a De Koningh, An 12, 191, cf Staveley, Chem Zeit 13, 1126) —5 Phenol may be titrated by adding standard NaOH to a solution containing s-tri-nitro benzene as indicator until a red colour appears (Bader, Fr 31, 58)

Salts—Phenol behaves as a very weak and It dissolves in KOHAq, but does not expel CO₂ from sodium carbonate in the cold—O₂H₂OK White hygroscopic needles, v. sol alcohol, ether, and water Oxidises rapidly in air—C₂H₂ONa* V₂Ields Ph₂O and C₁H₁₀O when distilled with NaPO₂ (Niederhäusern, B 15,

8 H

Sulphur at 200° gives S2(C2H4OH)2-Ba(OC₆H₆), Baq Crystalline crusts, got by bolling phenol with baryts water and evaporating in vacuo — Ca(OC₆H₆), Yields diphenylene oxide and a little benzene on distillation — Pb(OH)OC₆H₆ Made by boiling phenol with tharge (Calvert, C J 18, 68) — TiOC₆H₆. Trystals, al sol cold water (Kuhlmann, J 1864. Drystals, sl sol cold water (Kuhlmann, J 1864, 254) — $Hg(OC_4H_5)_*Hg_5Cl_24aq$ Pp got by adding mercurous chloride to a solution of NaOPh (Pouchet, C R 106, 276) — $Al(OC_6H_5)_s$ Made by heating phenol with aluminium and AlI, and by heating phenoi with aluminium and Ali, and pouring off the liquid product (Gladstone a Tribe, C J 89, 9, 41, 5, Hodgkinson, C N 1877, 237) Split up on distillation into Al₂O₈ and Ph₂O, other products being phenoi and a ketone C₁₈H₁₆O [97°] (c 280°), V.D 182 2 — Aniline salt C₂H₂ONH₂Ph [37°] (181°) Formed by boiling aniline with phenol (Dale a Schorlemmer, A 217, 388, Dyson, C J 43, 466, Mylins, B 19, 1002) Tables (from alcohol) — p-Toluidine salt C₆H₅ONH₅C₆H₄Me [81°] Needles (from ligroin) (Dyson)

Combinations —1 With SO, phenol forms

an unstable compound which may be distilled at 140° (best in a current of SO₂), and which crystallises in rectangular tablets If exposed to air it absorbs water and gives off SO₂ The compound melts between 25° and 30° (A Hölzer, J pr [2] 25, 463) —2 With CO₂ If salicylic acid be heated in a sealed tube for two hours at 260° it is resolved into phenol and CO2, but on cooling crystals resembling common salt with sides like staircases are formed. These melt at 37° They are decomposed by heat, and also by water, alcohol, ether, and chloroform, mto phenol and ${\rm CO}_2$ (A Klepl, J pr [2] 25, 464) The same compound is got from phenol and

liquid CO2 (Barth, A 148, 49)

Formyl derivative C. H.O CHO Liquid, boiling with decomposition at 180° (Seifert, J pr [2] 31, 467)

Acetyl derivative C6H5OA0 acetate (195°) at 733 mm (Orndorff, Am 10, 368) Formed by boiling an alcoholic solution of phenyl phosphate with KOAc (Williamson a Scrugham, A 92, 317, Kreysler, B 18, 1716) and by the action of AcCl on phenol (Cahours, 4 92, 816) or of POCl, (1 mol) on phenol (8 mols) mixed with HOAc (3 mols) (Nencki, *J pr* [2] 25, 282, Seifert, *J pr* [2] 31, 467) Obtained also by boiling phenol with acetamide (Guareschi, 4, 171, 140) A 171, 142) Heavy oil, saponified by KOHAq Reactions—1 Sodium acts violently, giving off and forming EtOAc, phenol, salicylic acid, C₁₀H₁₂O₂ [48°] crystallising from alcohol in needles, and C₁₀H₁₄O₄ [138°] nearly insol alcohol, but crystallising therefrom in yellow needles (Hodgkinson a W H Perkin, jun, C J 87, 487, 721) —2 Benzyl chloride after heating for 14 days leaves an oil with strong blue fluorescence which when saponified by alcoholic potash forms C₁₈H₁₀O [39°] (c 295°) and benzylphenol C₁₈H₁₂O [31°] (321°) (H a P)—3
Benzyl chloride and AlCl₂ give HCl, toluene, anthracene, Ac₂O, and CH₂Ph C₂H₄OAc—4
NaSEt forms PhONa and EtSAc (Seifert)—5 PCl, at 100° gives phenyl phosphate and C.H.O Coll Col. [26°] (Michael, Am 9, 207) —6 Chlorine in the cold forms A-Cl, p-chloro-phenol, and C_eH₄Cl(OAc) Chlorine at 160° yields AcCl,

CsH2Cl2(OAc), and mono- and di- chloro phenols (Seelig, J pr [2] 89, 175) —7 Bromine forms AcBr and C_cH_cBr OAc Excess of Br gives C_cH_cBr₂OH and C_cH_cBr₂OAc (Seelig) —8 BzCl and a little ZnCl₂ give PhOBz (Doebner, A

Proposity derivative C.H.O.CO Et [20°] (211°) S.G. 410648, 45 10642 Formed by distilling phenol with excess of propionyl chloride (Perkin, O.J. 55, 546) Large transparent prisms PCl, at 100° followed by water gives olly C_sH_sCl₂O (116°) (Michael, Am 9, 212) Butyryl derivative C_sH₅O CO

C,H,O CÓ C,H, (228°) S G 2 1 0364, 151 0269 F phenol and butyryl chloride (P3rkin) Formed from

Bensoyl derivative C₆H, OBz Phenyl bensoite [69°] (314° cor) HF 61,804 (Stohmann, J pr [2] 36,7) Made by melting benzoic acid (11 g) with phenol (10 g) and gradually adding POCl₆ (13 g) The product is washed with dilute KOH and crystallised from dilute alcohol, the yield being fav. (13 g) dilute alcohol, the yield being fair (12 g) (Rasiński, J pr [2] 26, 62, cf Ettling, A 53, 87, Stenhouse, A 53, 91, Laurent a Gerhardt, A 75, 75, List a Limpricht, A 90, 190) Formed also by boiling phenol with benzamide (Guareschi, A 171, 141) and from phenyl phosphate and NaOBz (Kreysler, B 18, 1719) Monoclinic prisms (from ether alcohol) Not saponified by boiling aqueous KOH, but saponi fied by alcoholic potash

Salicyl derivative v O OXY BENZOIC

Methyl derivative C₆H, O Me ² Ansole
Mol w 108 (155°) VD 379 (calc 373)
SG § 10110 (Pinette, A 243, 34), ½ 997
(Vincent, Bl [2] 40, 106) CE (0°-10°) 00083
SV 125 2 (R Schiff, A 220, 105) SH 405 at 0° (Schiff, A 234, 300) R_{∞} 55 33 (Nasını a Bernheimer, G 15, 93) H F p 15,860 H F v 13,830 (Thomsen, Th), 32,718 [C,O₂=94,000, $H_2, O = 69,000$] (Stohmann, J pr [2] 35, 23) Formed by distilling anisic acid or the methyl derivative of salicylic acid with baryta (Cahours, A Ch [3] 2, 274, 10, 353, 27, 439) Made also by heating PhOK with MeI at 110° (Cahours, A 78, 225) Prepared by heating NaOPh at 200° in a rapid current of MeCl (Vincent, Bl [2] 40, Oil with pleasant odour, v sol alcohol and ether Conc HIAq at 140° splits it up into phenol and MeI (Graebe, A 139, 149) At 400° it de composes into phenol and ethylene (Bamberger, B 19, 1820) Chlorine in the cold gives rise to [1 2]O₆H₄Cl OMe (c 200°), [1 3 6]O₆H₃Cl₂OMe, 12 20°6H, OI OME (C 200°), [1 3 6]C,H,CI,OMe, [28°], (233°), and [1 3 5 6]C,H,CI, OMe [60°] (249°) In presence of iodine, chlorine forms [1 2 3 5 6]C,HCl, OMe [100°] (279°) and also C,Cl, OMe [107°] (c 289°) Chlorine with I at 60° forms C,Cl, [220°], C,HCl, [87°] and C,H,Cl, [136°] Chlorine with I acting on boiling anisole forms (C,I) (C)Cl,HCl and some (CI). forms C₆Cl₆, COCl₂, HCl, and some CCl₄ Chlorine with SbCl, forms C₂Cl, OH [187°] and CCl, Chlorine with SbCl, at 100° gives C₂Cl,O [107°] (Hugounenq, A Ch [6] 20, 504) AcCl in CS, in presence of AlCl, forms CH, CO C, H, OMe (Gattermann, B 22, 1129), BzCl acts in like

Ethyl derivative C.H.OEt 'Phonetole. (172°) SG § 9822 (Pmette, A 248, 35). VD. 4 27 (calc. 4 21) CE (0°-10°) 00087. SV. 148 5 (R Schiff, A 220, 105) SH 429 (Schiff,

4 284, 300) H F.p 39,775 (Stohmann) Formed by distilling barum ethyl salicylate and by the action of EtI on C₆H₃OK (Cahours, A Oh. [3] 27, 463, Baly, A 70, 269) Formed also by the action of alcohol and ZnCl, on phenol (Kastropp, B 10, 1685) and by the action of dry alcohol on diszobenzene nitrate or sulphate (Remsen a Orndorff, A14. 9, 392)

Preparation — Equal volumes of H₂SO, and alcohol are mixed and allowed to cool liquid is then neutralised with soda and evaporated until Na2SO, begins to crystallise out The liquid is poured off from the crystals, mixed with a strong solution of sodium phenylate, and hea ed in an autoclave at 150° under 7 atmo spheres' pressure The sodic phenylate is made by dissolving phenol in caustic soda solution (SG 133) In calculating the amount of phenol it is assumed that half the alcohol forms sodio

ethyl sulphate (Kolbe, J. pr. [2] 27, 425)

Properties—Oil Yields with fuming HNO. a di nitro derivative [87°] At 400° it yields phenol and ethylene BzCl in CS₂ in presence of AlCl, forms C₆H₅ CO C₆H₄ OEt, AcCl acts in

like manner (Gattermann, B 22, 1129)

Propyl derivative CH, OPr (191°) SG § 9639 CE (0°-10°) 00086 SV 172 (Pinette, A 243, 35) H F p 46,574 (Stohmann) Isopropyl derivative PhOPr (176°) S G ⁹ 958 (Silva, Z 1870, 249)

Butyl derivative C,H,O C,H, (210 S G 0 95 C E (0°-10°) 00089 S V 195 8 (210°)C₆H₅ O CH₂Pr Isobutyl derivative

(198°) S G 12 939 (Riess, B 3, 780) Isoamyl derivative C,H, O C,H,

(225°) Formed from PhOK and isoamyl iodide (Cahours, C R 32, 61) Oil, lighter than water Heptyl derivative C,H, O C,H, (267°) S G \(\frac{0}{0} \) 9319 CE (0°-10°) 00091 S V 270 8 Octyl derivative C₈H, O C₈H₁, (283°) † § 9221 CE 00084 SV 2961 (Pinette,

SG 9 9221 CE 00084

A 243, 36)

Vinyl derivative CeH, O C2H3 (c 155°) SG 2 992 From the bromo ethyl derivative and alcoholic potash (Sabanéeff, Bl [2] 41, 253)

Bromo vinyl derivative CoH, O C2H2Br Formed from CH₂Br₂, phenol, and alcoholic potash (Sabanéeff, A 216, 277) Oil, decomposed by distillation

Di bromo vinyl derivative C₄H₄O C₂HBr₂ [38°] Got from phenol, C₂HBr₃, and alcoholic potash Gives PhO C₂HBr₄ [59°]

Tri-chloro vinyl derivative C.H.O CCI CCL. [26 5°] (106° at 12 mm) Formed by the action of PCl, upon phenyl acetate Also obtained by the action of potas sum phenol upon per chloro ethylene Crys talline solid Volatile with steam (Michael, B talline solid

19,845, Am 9,207)

Bromo-ethyl derivative PhOC.H.Br [39°] (240°-250°) Made from ethylene bromide and sodium phenol in alcoholic solution by digesting for 3 hours at 100° Separated from the ethylene-ether, (PhO)₂C₂H₄, by distilling with steam, in which it is much more volatile Colourless crystals with characteristic odour, partly decomposes on boiling V sol alcohol and ether (Weddige, J pr [2] 24, 242) Reactions — 1 Heated at 110° with alcoholic NH, it gives crystals of HN(C2H, OPh)2HBr, [216°], sl sol alcohol Alkalis liberate from Bromo-,

this salt the free base imido di-ethylene di phenyl ether as an alkaline oil. With HCl it forms a salt, HN(C,H,OPh),HCl [218°] It also forms a nitrate [197°] —2 With σ nitro phenol potassium it forms Ph O C,H,OC,H,NO, orys tallising in prisms, [86°] —3 Heated with potas sium p oxybenzoic ether in alcoholic solution it forms C₆H₅O C₂H₄O C₆H₄CO₂Et [81°], which, when saponified by alcoholic potash, yields the acid, C₆H₅ O C₂H₄ O C₆H₄ CO₂H melting at [196°] (Wagner, J pr [2] 27, 227)

Chloro-ethyl derivative PhO C₂H₄CI.
[25°] (221°) Made from C₂H₄CIBr and KOPh

Reacts with KOEt forming PhO C2H, OEt (230°), S G 11 1018 (Henry, C R 96, 1233), or (252°), S G 2 1 037 (Sabanéeff, Bl [2] 41, 253)

Penta-bromo ethyl derivative Phoc₂Br₅ [103°-106°] From the di bromo vinyl derivative by successive treatment with al coholic potash and Br (Sabanéeff, A 216, 282)

Methylene derivative CH2(OPh)2 (294°) Henry), (299°) (Arnhold, A 240, 201) SG

12 1114 (H), 2 1092 (A) Formed from

CH₂Br₂ and KOPh (Henry, A Ch [5] 36, 269)

Ethylene derivative C₃H₄(OPh), [98 5°]

(Burr, Z [2] 5, 165), [95°] (Luppmann, C C 1870, 45) Made from C₂H₄Br₂ and KOPh at 140° Crystals, al sol alcohol Br yields C₁H₄Br₂O₂ [C 100°] H₂SO₄ yields a disulphonic acid, whence C2H4(O C6H4SO2)2Pb may be got, crystallising from hot water in laminæ

Bromo propyl derivative C₈H₅O CH₂ CH₂ CH₂Br (246°-256°) from phenol, trimethylene bromide, and NaOEt (Lohmann, B 24, 2632) Oil Alcoholic NH, at 100° forms (PhO C₂H_e), NH which distils above 300° and gives B'HCl [206°], and the nitros amine (PhO C₂H_e), NNO [61°] Aniline forms PhO C H NHDL 1200° above 100° and 10 PhO C, H, NHPh [32°] which gives B'HCl [170°] With NaOMe in MeOH it yields PhO C, H, OMe (231°), while alcoholic potash solution forms PhO C₃H₆ OEt (329°, or probably 239°) The compound PhO C₃H₆ OH (250°) is formed by the action of nitrous acid on PhO C.H. NH. (242°) which is itself obtained by the hydrolysis of PhO C₃H₆ NH CO C₆H₄ CO₂H

Trimethylene derivative CH₂(CH₂OPh)₂ [61°] A by product in the preparation of the bromo propyl derivative

Allyl derivative PhO C,H, (19) From C,H,Br and NaOPh (Henry, B 5, 455)

De chloro allylderivative PhO C.H.Cl. (114°-118° in racuo) Got from PhO CO Et

and PCl, (Michael)

Bromo allyl derivative PhO C.H.Br (240°) Got from CH₂ CHBr CH₂Br and KOPh Henry, Bl [2] 40, 324) Alcoholic potash forms the propargyl derivative (210°)

Bensyl derivative v Phenyl ether of

BENZYL ALCOHOL

Glucoside CaH,O CaH,(OH), CHO Formed by adding acetochlorhydrose to an alcoholic solution of PhOK (Michael, C R 89, 355, Am 1, 306) Long needles (from hot water), v sol water, sol alcohol and HOAc H.SO, forms Acetic anhydride and yellow solution NaOAc at 100° yield the tetra acetyl derivative C,H,O C,H,(OAc), CHO, which crystallises from alcohol in long white needles

References — AMIDO, AMIDO DI-IMIDO-, Bromo amido-, BROMO IODO-NITRO-,

3 H 2

BROMO-NITRO-, CHLORO-, TRI-CHLOBO-IODO-. CHLORO-MITRO-, IODO-, DI-IODO AMIDO-, IODO-NITEO-, and NITEO- phenols

Diphenol v Dr-oxy-DIPHENYL. Tetraphenol v FURFURANE

PHENOL-AZO-COMPOUNDS v Oxy-bensene-AZO- COMPOUNDS

Phenol-bidiago- compounds v. DISAZO COM-POUNDS

PHENOL-BLUE v Dr-methyl amido phenylunide of QUINONE

PHENOL CARBOXYLIC ACID v OXY-BENZOIC

Phenol dicarboxylic acid v Oxy PHTHALIC, OXY-ISOPHTHALIC, and OXY-TEREPHTHALIC ACIDS

Phenol tricarboxylic acid v Oxy-TRIMESIO

PHENOLISATIN v DI-OXY DIPHENYLOXIN-DOLE

PHENOL-PHTHALEIN C20H11O4 26

 $C_0H_4 < COOO^{C}(C_0H_4OH)_2$ [c 253°] Formed by heating phenol with phthalic anhydride and conc H₂SO, Obtained also from di-amido-di-phenylphthalide by the diazo-reaction (Baeyer, A 202, 36, B 9, 1230, 12, 642) Small crystals (from alcohol), v sol hot alcohol, sl sol water Its solutions in alkalis and alkaline carbonates are red, but become colourless on neutralisation, and also on addition of excess of KOHAq but not by NH. The red colour of a solution in very dilute ammonia disappears on standing (Long, Am 11, Aniline does not give any colour with

phenol-phthalein AgNO, gives a violet pp

Reactions—1 H₂SO, at 100° forms a sulphonic acid, but at 200° it yields oxy-anthraquinone -2 PCl, yields di-chloro di phenyl phthalide [156°] -3 Zinc-dust and NaOHAq yield phenol-phthalin CO₂H C₆H₄ CH(C₆H₄OH)₂ 4 Potash fusion gives dioxybenzophenone and benzoicacid -5 NH, Aq at 170° forms C20H16N2O2

[266°] Di-acetyl derivative C20H12Ac2O4 [143°]

Colourless tables (from wood spirit)

Anhydride $C_{20}H_{12}O_{2}$ [175°] A by product in the preparation of phenol-phthalein (Baeyer, A 212, 347) Needles, insol NaOHAq Conc H2SO, forms a solution with green fluor-Bromine yields $C_{20}H_{10}Br_2O_2$ [258°] Alcoholic potash and zinc dust reduce it to phthalin C₂₀H₁₄O₃

 $\mathrm{C_{20}H_{10}Br_4O_4}$ Tetra bromo-phenol phthalein $C_0H_4C_2O_2(C_0H_2Br_2OH)_2$ [220°-280°] Formed by adding Br in HOAc to a solution of phenol phthalein in alcohol Colourless needles (from ether), sl sol alcohol and HOAc Alkalis form violet solutions, decolourised by H₂SO₄ produces di bromo-oxy-anthra quinone on heating to 150° Ac O yields a diacetyl derivative [134°] H₂SO₄ containing KNO₄ forms bromorosoquinone C₁₂H₄Br₄O₂, sepa rating from alcohol chloroform in red crystals with steel-blue lustre, insol water, forming a violet solution in H2SO4, and converted by boilwhence nitrous and produces $C_{20}H_{12}Br_{4}O_{2}$ [264°] whence nitrous and produces $C_{20}H_{12}Br_{4}N_{2}O_{2}$ [241°] PHENOL-PHTHALIDEIN $C_{20}H_{12}O_{2}$ $C_{20}H_{12}O_{2}$

C,H, COO C,H,OH,OH) Dr-oxy-

pnenyi-oxanthranol [212°]. Formed by oxida tion of phenol-phthalidin by dilute alkaline KMnO₄ (Baeyer, A 202, 100) Monoclinic tables (from HOAo), a b c = 46 1 49, β = 69° 5′, v sol alcohol and acetone. It forms a pale-yellow Monoclinic tables solution in KOHAq, and is reppd by HCl Conc H.SO, forms a violet solution, and on heating produces oxyanthraquinone and p thalic acid Reduced by zinc-dust and NaOHAq to phenoi phthalidin PCl, yields di-chloro phenyl-ox anthranol C₂₀H₁₂Cl₂O₂ [156°]. Bromine gives C₂₀H₁₂Br₄O₄ [above 280°], whence C₂₀H₂Ac₂Br₄O₄ [182°] may be obtained On adding phenos to a solution of phenol-phthaliden in F₂SO₄, the violet colour changes to blood-ied, and on a ldi tion of water a red amorphous pp is thrown down. This pp forms a deep-violet solution in alkalıs, and yıelds a crystallıne bromo-derivative A mixture of NH₂Aq and alcohol at 160° converts the red pp into $O_{20}H_{15}NO_{2}$ [260°], crystallising in yellow needles

Acetyl derivative $C_{20}H_{12}Ac_2O_4$ [109°] Monoclinic prisms, a $b c = 2.78 \cdot 1 \cdot 1 \cdot 44$, $\beta = 77^{\circ}$ 2° PHENOL-PHTHALIDEIN CHLORIDE

DI-CHLORO PHENYL-OXANTHRANOL

PHENOL-PHTHALIDIN v DI-OXY-PHENYL ANTHRANOL

PHENOL-PHTHALIN C20H16O4 2 &

CO2H C6H, CH(C6H4OH)2. Di oxy-tri phenyl-[225°] Formed by methane carboxylic acid reduction of phenol-phthalein with zinc-aust and NaOHAq (Baeyer, A 202, 80, 212, 350) Forms a colourless solution in Small needles potash, coloured red by K_sFeCy_s through forma tion of phenol phthalein Yields a di acetyl derivative [146°] Sodium-amalgam yields Sodium-amalgam yields CH (OH) C₆H₄ CH(C₆H₄OH)₂ phenol-phthalol [190°], which gives a tri-acetyl derivative [40°

Anhydrade $O_{20}H_{14}O_{3}$ [217°] Formed by reducing the anhydride of phenol-phthalein Small needles (from dilute alcohol)

Dı-chloro-phenol-phthalın Anhydride O<0,H,Cl C,H,Cl>CH C,H, CO,H [226°-230°] Got by the action of zinc and NaOHAq on the com pound C₂₀H₁₀Cl₂O₃ derived from fluorescein (v vol 11 p 558) Small needles (from dil alcohol)

Tetra-bromo-phenol-phthalin CO₂H C₆H₄ CH(C₆H₂Br₂OH)₂ [205°] Formed by bromination Crystals (from benzene) Yields a di-acetyl derivative [166°] (Baeyer, A. 202, 80) Conc. H₂SO₄ converts it into tetra bromo phenol phthalidin C₂₀H₁₀Br₄O₂, which crystallises from alcohol in golden needles, and is converted by oxidising agents into tetra bromo-phthalidein C₂₀H₁₀Br₄O₄ Tetra-bromo-phenol phthalidin is tetra-bromo di-oxy phenyl-anthranol, and its diacetyl derivative crystallises in needles [256°]

PHENOL-QUINOLINE QUINOLINE

PHENOLS Compounds containing hydroxyl united to carbon, which forms part of a benzene nucleus (v Benzene and Alcohols) They much resemble the tertiary fatty alcohols, being more acid in character than primary alcohols phenols and tertiary alcohols form hardly any acctate on heating with HOAc Phenols in acetate on heating with HOAc Phenols in which hydrogen in the o-or p-position has been displaced by NO, or by a halogen are even more strongly acid in character (e.g. pieric acid)

Formation.—1. By potash-fusion from sul-

phonic acids —2 By the diazo-reaction from amido-compounds (v Diazo-compounds) —3 By distillation of oxyacids either alone or with lime —4. Halogens in a benzene nucleus may sometimes be displaced by hydroxyl by heating with KOHAq in sealed tubes, thus o- and p-chloro-nitro benzenes give o- and p-nitro phenols

by this treatment

Properties of Phenol and its homologues — Dissolve in NaOHAq but not in Na₂CoAq Phenols do not give rise on oxidation to an acid or sidehyde containing the same number of atoms of carbon, in the molecule They do not exchange H 'or K on treatment with KSH, nor do they form ammonium salts They do not react (like alcohol) with HCl FeCl, colours aqueous solutions of phenols, and products of oxidation are often produced. H₂SO, to which 6 p c of KNO, has been added gives with a solution of a phenol in H₂SO, a brown colour, changing on warming to green and blue (Liebermann, B 7, 248, 806, 1098)

Reactions -1 Readily undergo bromination, chlorination, and nitration -2 H.SO, forms sulphonic acids, the isomeric sulphuric acids being very unstable -3 Sodium and CO, form oxyacids on heating (Kolbe)—4 Chloroform and NaOHAq form, on boiling, oxy-aldehydes (Tiemann a Reimer, B 9, 824)—5 CCl, and alcoholic potash at 100° form oxyacids— 6 Ammoniacal ZnCl, at 200°-300° converts phenols into amines (Merz a Weith, B 13, 1298, 20, 544) -7 Solutions of NaHCO, and (NH4)HCO, yield oxyacids on heating with dioxyphenols (Kostanecki, B 18, 3203) -8 Distillation over sinc-dust reduces the hydroxyl to hydrogen, forming the corresponding hydrocarbons -9 Alkoyl chlorides and anhydrides yield alkoyl derivatives of phenols, especially if a little powdered zinc be added (Schiaparelli, G 11, 69) When an alkoyl chloride is used oxy ketones are also often formed through the alkoyl entering the benzene nucleus -10 Organic acids mixed with phenols readily yield alkoyl derivatives of the phenols on adding POCl, or on heating in presence of ZnCl₂ (Rasınskı, *J pr* [2] 26, 62, Nenckı, *M* 10, 906) Alcohols in presence of ZnCl₂ form alkyl ether and higher homologous phenols — 11 Alkyl derivatives of phenols split up on distillation into phenols and olefines (Bamberger, B 19, 1819) -12 The acid sulphuric ethers of the form C₂H₄X O SO₄H derived from o and p- alkyl-phenols are oxidised by alkaline KMnO, to o- and p- oxy benzoic soids (Heymann, B 19, 704) —13 Alkaline solutions of phenols absorb atmospheric oxygen, forming dark coloured products—14 Homologues of phenol frequently yield oxyacids on fusion with potash, the alkyl side-chain being oxidised to carboxyl 15 Aldshydes in presence of dehydrating agents form compounds of the form XCH(OY), which change to XCH(Y"OH). Thus (8) naphthol give PhCH(OC, H,) and benzoic aldehyde changing to PhOH(O10HOH)2, which is at once converted into the anhydride PhCH CieHe>0 (Baeyer, B 5, 26, Claisen, B 19, 3316).— 16 Phthalyl chlorids usually forms phthalic

acid displaces hydrogen in the c- or p- position by nitrosyl The products are identical with the mono-oxims formed by warming quinones with hydroxylamine hydrochloride, but yield nitrophenols on oxidation with alkaline K_FeCy_—19 Diazo salts readily form azo-compounds (p v) 20 Diazo-amido-compounds form oxy azo-compounds Thus C_H_Cl N_NHC_H_Cl heated with phenol on a water bath yields C_H_Cl N_C_H_OH and C_H_ClNH_ (Heumann a Occonomides, B. 20, 904)—21 Benzoirchloride acting on phenoly in which there is an atom of hydrogen in the p position to hydroxyl yields coloring matters related to aurin (Doebner, A 217, 223, 257, 56) PHENOL O-SULPHONIC ACID C_H_SO_4 26

PHENOL O-SULPHONIC ACID C.H.,850. 2.6 C.B.H.(OH) SO.H Formed, together with the p acid, by the action of H.2SO. on phenol, especially in the cold (Kekulé, Z 1867, 199, B. 2, 330, Faust, Z 1871, 339, Armstrong, C J 24, 1112, 25, 12, 857) Prepared by dropping H.2SO. on dry phenol at -10°, allowing the product to stand for a week, and then distilling, treating with BaCO. and KHCO. successively, and crystallising the K salt (Allain le Canu, C R 109, 225) Crystals (containing 1½ aq), melting at 50° and decomposing at a higher temperature, with liberation of H.2SO. Sol ether When heated with water it changes to phenol p-sulphonic and (Post, A 205, 64) Possesses powerful antiseptic properties (Serrant, C R 102, 1079)

Reactions — 1 Potash-fusion gives some pyrocatechin — The action begins about 280° and attains a maximum (20 pc) at 320° Sodatision also gives pyrocatechin — The action begins at 310° At 330° the yield is 6 pc Fusion with a mixture of potash and soda gives a still smaller yield (1 pc) of pyrocatechin (Degener, J pr [2] 20, 308) — 2 Bromine-vapour acting at —8° on the K salt yields bromo and di bromo derivatives — 3 BzCl forms PhOBz on heating with the K salt (Solommanoff, Z [2] 5, 296) —4 Heated with dilute HCl at 140° it is split up into phenol and H₂SO₄ (Armstrong)

Salts—KA'2aq [235°-240°] Colourless trimetric prisms, sol water—NaA'1\frac{1}{2}aq —BaA', aq needles S 25 at 100°—BaA', 2aq —PbA', aq tables, sl sol water—The aniline salt yields phenol and amido-benzene 2-sul phonic acid on distillation (Kopp, B 4, 978)

phonic acid on distillation (Kopp, B 4, 978)

Methyl derivative C.H.(OMe) SO.H

Formed from the acid, KOH, Mel, and MeOH

(Kckulé) — KA' aq needles, more soluble than

its p-isomeride (Haitinger, M 4, 173) Yields a

chloride [55°]

Ethyl derivative Forms a K salt crystallising in plates

Phenol m-sulphonic acid C_sH_s(OH) SO_sH
Formed by potash-fusion from benzene m- or pdisulphonic acid (Barth a Senhofer, B 9, 969)
Needles (containing 2aq) FeCl_s gives a violet
colour Yields resoroin on fusion with potash
—NaA'aq —KA'aq [200°-210°] Efflorescent
needles —K_sO_sH_sSO_sQ_s—PbA'_sSaq. tables, v
sol water—BaA'_sIaq —CuA'_s6aq green tables

Ethyl derivative C_sH_s(OEt) SO_sH. Got
by the action of KOH and Eti on the acid (De-

Ethyl dersvative C.H. [OEt) SO.H. Got by the action of KOH and Eti on the acid (Deliser, B 5, 26, Claisen, B 19, 3316).—

16 Phthalyl chloride usually forms phthalic ethers (B Meyer, B, 24, 2600).—17 Iodine and potash give di- and tri- iodo- derivatives (Messinger a. Vortmann, B. 22, 2315).—18. Nitrous

Ethyl dersvative C.H. [OEt] SO.H. Got by the action of KOH and Eti on the acid (Delise a Lagai, B 23, 3893) Deliquescent needles Yields a chloride [38°] and an amide potash give di- and tri- iodo- derivatives (Messinger a. Vortmann, B. 22, 2315).—18. Nitrous

Phenol p-sulphonic acid C.H.(OH) SO.H Formed by warming phenol with H₂SO₄ or ClSO₂H. Formed also from amido benzene psulphonic soid by the diazo- reaction Highly deliquescent hydrated needles (Le Canu, CR

Reactions -1 Bromine acting on a cold solution forms mono- and di-bromo- derivatives and finally trabromo-phenol (Le Canu)—2 Boiling HIAq gives phenol (Benedikt a. Bamberger, M 12, 4) -3 Potash fusion forms a little resorcin (Lincke, J pr [2] 8, 43) -4 PCl, gives p-di chloro benzene and C₈H₄Cl O POCl₂ (Kekulé, B 5, 875, 6, 943) —5 MnO₂ and H₂SO₄ yield quinone (Schrader, B 8, 759) —6 Dilute HCl at 150° forms phenol and H₂SO₄

Salts -- KA' [400°] Six sided trimetric Salts—KA' [400°] Six sided trimetrio lamella a b c = 879 1 1 002 —NaA' 2aq monoclinic prisms (Shadwell, J 1881, 874) — BaA', 3aq S 50 at 100° —BaC,H,SO, 2aq —PbA', 2aq —CoA', 28aq (Freund, A 120, 85) — NiA', 28aq —CuA', 210aq —AgA' —Aniline salt Plates [170°] Decomposed at 190° into heavel and small benzer a gulphong and phenol and amido benzene p sulphonic acid — o-Toluidine salt [c 192°] S 10 7 at 14° (Lecco, J 1874, 747) - p Toluidine salt [202°] S 52 at 17°

Benzoyl derivative C₆H₄(OBz) SO₃H Formed from PhOBz and SO₃ (Engelhardt a Latschinoff, Z 1868, 76)—KA' long needles (from water)—CaA'₂—BaA'₂—PbA'₂2aq—

CuA', 6aq -AgA'

Methyl derivative C.H. (OMe) SO.H Got by methylation The K salt forms needles C,H,(OEt) SO,H derivativeFormed from the acid, KOH, and EtI (Kekulé, Z 1867, 200), and also, together with the o- iso meride, by sulphonating phenetole (Lippmann, OR 68, 1832) —BaA', 4aq crystals, v sl sol hot water —KA' aq needles (from alcohol) Phenyl ether PhA' Formed from phenol

(2 mols) and ClSO₃H (Engelhardt a Latschinoff, Z 1869, 298) Syrup, split up by water

into phenol and phenol sulphonic acid

Anhydride C₁₂H₁₀S₂O₇ Formed from the acid and POCl₂ (Schiff, A 178, 171) Powder, v sol water, v sl sol HClAq Coloured violetred by FeCl, Ppts gelatin and alkaloids Yields

an acetyl derivative C₁₂H₄AcS₂O₇
Phenol disulphonic acid C₆H₂(OH)(SO₂H)₂ [124] Formed by warming phenol with H.SO and SOs, and by allowing separate vessels of phenol and fuming H₂SO₄ (S G 185) to remain for six months in vacuo, the acid absorbing the vapour of phenol (Kekulé, Z 1866, 693, Le Canu, C R 109, 442) Formed also from diazobenzene sulphate and fuming H₂SO₄ (Griess, A 137, 69, Armstrong a Prevost, B 6, 664) Nodular groups of deliquescent needles, v e sol water and alcohol HNO, yields pierie acid Potash fusion gives pyrocatechin and its sul-phonic acid, soda fusion forms also proto-catechine acid (Barth a Schmidt B 12, 1260).

FeOl, gives a red colour (Stadeler, A 144, 299)
Salts — K₄A" aq Needles, decomposing about 270° S 33 at 100° — Bah" 4aq S 19 6 at 15° — Ba₁(C₂H₁S₂O₂), 6aq — Ba₂(C₂H₂S₂O₂) ag Sl. sol water — $P_{1}(O_{2}H_{2}S_{2}O_{2})$ 6aq Sl. sol water — Ag₂A" plates, v sol water

Methyl derivative C.H. (OMe)(SO.H). Formed by sulphonation of amsic acid (Zervas,

A 103, 342), and also from SO₂(C₆H₄OMe), and cone H₂SO, at 170° (Annaheim, A 172, 47) -

BaA" 4aq monodinic crystals

Ethyl derivative C_cH₁(OEt)(SO₂H),

[1 2 4] Formed from amido benzene disulphonic acid by the diazo- reaction (Zander, A 198, 25) Very deliquescent needles Yields a chlorid [108°] and an amide [233°] — KHA" aq — BaA" 2aq — BaA" 3aq v sol water Yields a chloride

Ethylene derivative C₂H₄(O C₄H₄ SO₄H)₂. Formed from C₄H₄(OPh)₃ and H₂SO₄ at 120° (Luppmann, Z 1869, 447) —

BaA" xaq —PbA" xaq plates, meal cold water Phenol disulphonic acid An unstable and is formed by heating the trisulphonic acid with KOH (3 pts) and some water at 150° (Senhofer, J 1879, 749) Yields K₂A" 3½ aq —BaA" 4aq —

PbA'' 4aq long prisms, v sol water Phenol trisulphonic acid C₂H₂(OH)(SO₂H), [1 2 4 6] Formed by heating phenol (6 pts) with H₂SO₄ (30 pts) and P₂O₅ (15 pts) at 180° (Senhofer, A 170, 110) Formed also by heating SO₂(C₆H₄ OH)₂ with fuming H SO₄ at 190° (An naheim, A 172, 28) Needles or short prisms (containing 3\frac{1}{3}aq) Coloured red by FeCl₃—
Na₃A''' 3aq — K₂A''' 4aq — K₄C₆H₂S₂O₁₀ 2aq —
Ba₃A'''₂ 4aq scales — Ba₂A'''₂ 10aq plates —
Cd₂A'''₂ 7aq — Pb₄C₆H₂S₂O₁₀(OH), 4\frac{1}{2}aq crystal
line powder — Ag₃A''' 1\frac{1}{2}aq slender needles

References -AMIDO-, BROMO, BROMO NITES. DI 10DO, IODO NITRO PHENOL SULPHONIC ACIDS

PHENOQUINONE C18H1 O4 [71°] Formed from phenol (1 mol) and quinone (2 n.ols), or by boiling phenol with aqueous CrO, (Wichel haus, B 5,248,846, Nietzki, A 215,134, Hesse, A 200, 232, Erhart, Ar Ph [3] 8, 481) Red needles with green lustre, sol cold water, alcohol, ether, and ligroin Reduced by SO, to hydro quinone Bromine forms di bromo phenol

PHENOSAFRANINE v SAFRANINE

PHENOSE C.H12O. Formed by the action of aqueous ClOH on benzene in the dark, the resulting C₆H₉Cl₃O₇ [10°] being extracted with ether and heated with very dilute Na,CO, (Carius, A 136, 323) Formed also by the electro lysis of toluene mixed with alcohol and dilute H.SO. (Renard, C R 92, 965) Deliquescent amorphous mass, v sol water and alcohol, insol. ether Has a sweet taste Decomposes above Turned brown by acids and alkalis Pre vents ppn of cupric sulphate by potash, and reduces Fehling's solution Does not undergo alcoholic fermentation Reduced by HI to hexyl nodide HNO, yields oxalic acid Ammoniacal

lead acetate ppts C.H.Pb.O.
PHENOXYACETIC ACID v Phenyl deriva twe of GLYCOLLIC ACID, vol 11 p 638, and

CHLORO-PHENOXYACETIC ACID

PHENOXYACETIC ACRYLIC ACID v Carb oxy methyl derwative of Coumaric acid PHENOXYACETIC-CARBOXYLIC ACID v

CARBOXYPHENOXYACETIC ACID

γ-PHENOXY BUTTRIC ACID C₁₆H₁₂O₃ * ε C₂H₄O CH₂CH₂CH₂CO₂H [60°] Made from the intrile and HClAq at 100° Silvery plates, insol water, v sol alcohol —AgA' white crystalline powder, decomposing at 200°

Nitrile Pho C.H. CN Formed from PhO C.H.Br, alcohol, and aqueous KCy (Lohmann, B. 24, 2640), and from γ-chlorobutyronitrile and NaOPh (Gabriel, B. 24 3231). White needles Conc H_2SO_4 converts it into $C_6H_4(SO_2H)$ O C_8H_6 CONH₂ [211°], a crystalline powder which gives BaA_2 as white crystals insol Aq Yields PhO C_4H_8 NH₂ (256°) on reduction

PHENPROPYL- COMPOUNDS v. PROPYL-PHENYL- COL YOUNDS

PHENPLOPYLAMINE AMIDO PHENYL-PROPANE

PHENUVIC ACID v PHENYL METHYL FUR-FURANE CARBOXYLIC ACID

The monovalent radicle C,H,. PHENYL It is more chlorous in character than methyl

Diphenyl C₁₂H₀ te C₄H₁ C₈H₂ Mol w 154 [70°] (254°) (Schultz, A. 174, 205), (253° at 716 mm) (Bamberger a Lodter, B 20, 3077) H C v 1,492,800 (Stohmann, J pr [2] 40, 86), 1,508,700 (Berthelot, Bl [2] 47, 865, A Ch [6] HCp 1,494,300 (S), 1,510,100 (B) 10, 448) $HF = 19,800 (\hat{S}), -37,100 (\hat{B})$ $\hat{S} \hat{V} \hat{S} = 154.25$ (Schiff) Occurs in the coal tar oils boiling at 200°-300° (Buchner, B 8, 22, Schulze, B 17,

Formation −1 By adding slices of sodium to bromo benzene and distilling after 24 hours (Fittig, A 121, 361, 132, 201, Schultz, A 174, 201, Engelhardt a Latschinoff, Z [2] 7, 259) — 2 From chloro benzene and sodium amalgam (Church, C J 16, 76) -3 With other hydrocarbons by passing benzene vapour through a red hot tube (Berthelot, Z 1866, 707), and formed consequently in many reactions in which benzene is produced at a high temperature -4 By passing benzene vapour mixed with SbCl, or SnCl, through a red hot tube (Watson Smith, C J 30, 30, Aronheim, B 9, 1898) -5 A product of the passage of azobenzene through red hot tubes (Claus, B 8, 37) -6 By the action of red hot zinc dust on di phenylene ketone-oxide 7 By heating diphenylene ketone dicarboxylic acid with lime (Bamberger a Hooker, A 229, 155)—8 From benzidine by the diazo-reaction (Griess, Tr 1864 [3] 692)—9 By heating phenol with K at 240° and ppg with water—10 By subjecting bromo benzene to an electric current, using zinc for the positive electrode (Christo manos, G 5, 402) -11 In small quantity in the decomposition of diazobenzene salts by alcohol (Griess) and by SnCl. (Culman a Gasiorowski, J pr [2] 40, 97)

Preparation -1 By slowly passing benzene through a red hot iron tube By successive passage of the unchanged benzene through the tube the yield may be raised to 97 pc of the theoretical (Adam, A Ch [6] 15, 224, cf Luddens, B 8, 870) -2 31 g and the are dissolved in 40 g conc. H.SO, and 150 g water, and diazotised with 81 g NaNO, 100 g 90 pc alcohol is then added, followed gradually by 50 g finely-divided copper After stirring for one hour it is finally distilled with steam The yield is 6-7 grms Iron and zinc-dust may also be used The temperature must not rise above 80°-40° (L Gattermann, B

23, 1226)

Properties —Indescent nacreous scales (from alcohol), v sol hot alcohol and ether

Reactions — 1 Readily yields di-bromo- and di-mitro-derivatives Chlorine, in presence of SbCl₁, yields C₁₂H₂Cl₂ (Kramers, A. 189, 14?) — 2 Heated in a stream of Cl in 1072)

presence of I the product is Circlin (Ruoff, B 9, 1048, of Merz a. Weith, B 16, 2881) -3 A mixture of diphenyl and ethylene passed through a red hot tube yields benzene, styrene, anthracene, and phenanthrene (Barbier, A. Ch. [5] 7, 582).—4 CrO₂Cl₂ in HOAc oxidises it to benzoic acid (Carstanjen, J pr [2] 2, 79) -5 AlCl. yields, on heating, benzene and a pitchy mass (Friedel a Crafts, C R 100, 692) Diphenyl (15 pts) heated with AlCl, (1 pt) and CH₂Cl₂ (10 pts) neated with AlCl₂ (1 pt) and CH₂Cl₂ (10 pts) yields diphenylene-methane (fluorene) [113°] and (C₄H₄, C₄H₄)₂CH₂ (310°-820°) (Adam, Bl [2] 47, 686) — 6 AlCl₂ and COCl₂ give (C₄H₄, C₄H₄, CO CH₂ [121°] —EtCl and AlCl₂ give C₄H₄, C₄H₄ (C CH₂, [121°] —EtCl and AlCl₂ give C₄H₄, C₄H₄ (C CH₂, [285°) and C₄H₃, C₄H₂Et₂ (a. 307°) In all these cases the compounds are m-

derivatives (Adam, A Ch [6] 15, 224)

Dihydride C₁₂H₁₂ (249°). Got by the action of boiling alcoholic potash on C₁₂H₁₄Br₂, which is formed from C₁, H₁₄ and Br (Bamberger a Lodter, B 21, 843) Oil, volatile with steam, a Lodter, B 21, 843) Oil, sol ether Yields $C_{12}H_{12}Br_{2}$

Tetra hydride C₁₂H₁₄ (245°) at 716 mm Got by reducing diphenyl dissolved in amyl alcohol with sodium (Bamberger a Lodter, B 20, 3077) Liquid Yields C12H1Br, and C12H1Br. [134°]

References — Amudo, Bromo, Bromo amido, Bromo nitro, Chloro, Di chloro di nitro, DI 1000, NITRO-, and Oxy-, DIPHENYL

PHENYL-ACETAMIDE v Acetyl derivative of Aniline and Amide of Phenyl-Acetic acid

PHENYL-ACETAMIDINE C.H. N. C.H. CH2 C(NH) NH2 Formed from the thio amide CH2Ph CS NH2 by the action of ammonia and atmospheric oxygen, or of ammonia and HgCl₂ (Bernthsen, B 8, 1319, 9, 429, A 184, 321) Formed also from CH₂Ph C(NH₂Cl) OEt and ammonia (Luckenbach, B 17, 1423) Crys tals, decomposed by heat, v sol alcohol, ether, Absorbs CO, from the air and warm water Decomposed by heating with water and alcohol

nto NH₂ and CH₂Ph CONH₂.

Salts —B'HCl aq — B'₂H₂PtCl₂ —B'H₂SO₄.

tables, v sol water and alcohol —B'₂H₂S₂O₂.

[198°] Needles (from alcohol) —B'HNO₃ Monoclinic crystals (Lossen, A 265, 165) —B'HOAc [193°] Stellate groups of needles (from alco-

hol) -B'2H2C2O4 prisms

Dr-acetyl derivative CeHs CH2 C(NAc) NHAc [1 [178°] Four sided tables (from water), al sol alcohol and ether

Phenyl - acetamidine CH, C(NPh) NH, Formed from acetonitrile and aniline hydrochloride at 170° (Bernthsen, A. 184, 358) Oil. B'H₂C₂O₄ v e sol water

s-Di phenyl-acetamidine C,4H,4N, CH, C(NPh) NHPh Ethenyl-dr-phenyl-amidine [132°] Formation —1 From aniline (8 pts). Formation -1 From aniline (8 pts), HOAc (2 pts) and POl₂ (2 pts) (Hofmann, C R. 62, 729) —2 From acetanlide (2 mols) and POl₃ (1 mol) (Lippmann, B 7, 541, Wallach, B 8, 1567) —8 From acetonitrile and aniline hydro chloride at 240° (Bernthsen).—4 By passing HCl into heated acetanilide (Wallach, B 15, 210) -5 By-product in the preparation of thio acetanilide from acetanilide and P.S. -6 By distillation of throacetanilide (Jacobsen, B 19,

Preparation -By heating a mixture of equal weights of acetanilide and aniline hydrochloride

Properties - Slender needles or thin prisms, al sol, alcohol, forming a neutral solution, nearly insol water, v. sol ether Conc H.SO, forms amido-benzene p sulphonic acid and acetic acid. Tin and HCl reduce it to aniline and HOAc Fuming HNO, forms the insoluble nitrate of a di mtro-derivative C_{1.}H₁₂N₄O_.HNO, [182°] (Biedermann, B 7, 540) COCl, at 60° forms C18H12N2O2Cl2, whence NaOEt yields C28H22N2O4 [91°] crystallising from ether (Loeb, B 18, 2427, 19, 2340) Excess of COCl₂ in benzene yields O1.H12N,O [118°], which is decomposed by dilute HCl into aniline and phenyl cyanate Cyanogen passed into an ethereal solution forms C16H16N4O, a white crystalline powder [1650 Etl yields only CH2.C(NPh) NPhEt, whence MeI followed by moist AgO produces strongly-alka hne CH₃ C(NPh) NPhEtMe(OH) — B'HCl tables, m sol water —B'2H2PtCl3 —B'HNO3
u-Di phenyl-acetamidine CH3 C(NH) NPh2

Formed from diphenylamine hydrochloride and acetonitrile by heating for a week at 150° (Bernthsen, A 192, 25) Monoclinic tablets or thick prisms, abc=114211222V sol alcohol, forming an alkaline solution CS₂ at 100° gives di phenyl-thioacetamide The hydrochloride is v e sol water -B'2H2PtCls -

B'HNCS Colourless tablets Dı phenyl-acetamıdıne

C.H. CH. C(NPh) NH. Phenyl phenyl acetam-dane [c 128°] Formed, with H.S. by heating C.H. CH. CS NH. with aniline hydrochloride (B) Formed also by heating phenyl-aceto-nitrile (benzyl cyanide) with annine hydro-chloride at 230° and by the action of iodine on a mixture of aniline and phenyl thioacet amide Small needles or laminæ, v sl sol water, v sol alcohol and ether May be sub limed Boiling dilute alcohol decomposes it into aniline and CH.Ph CONH.

Tri-phenyl-acetamidane

C.H. CH. C(NPh) NHPh [108°] Formed from C.H. CH. C(NH, Cl) OEt (1 mol) and alcoholic and me (3 mols) (Luckenbach, B 17, 1427) Plates (from alcohol) -B'₂H₂PtCl₃ plates

Reference - DI-BROMO DI PHENYL ACETAM IDINE

PHENYL ACETATE v Acetyl derivative of PHENOL

PHENYL-ACETCHLORAMIDE v Chloracet

andlide in the article Aniline

PHENYL-ACETIC ACID C₂H₂O₂ 2 e

C₂H₁ CH₂CO₂H Alphatoluylic acid Mol w

136 [77°] (265 5° cor) S G ²³ 1 0778, ¹²⁵

1 0384 H C p 933,200 (Stohmann, J pr [2]

40, 184). H C v 932,600 H F 94,800 (Stohmann), 59,000 (von Rechenberg)

Formation—1 By saponification of its metrile (Cannizzaro, A. 96, 246, C R 52, 966, 54, 1225) -2 By boiling vulpic acid with baryta water (Möller a Strecker, A 113, 64) -8 By reducing mandelic acid with cone HIAq and P (Crum Brown, Proc Roy Soc Edinb 5, 409) -4 By the putrefactive fermentation of proteids (Salkowski, B 12, 649, H 2, 420, 9, 507)

Preparation.—By converting benzyl chloride into the nitrile (benzyl cyanide), mixing 100 grms of the cyanide with 300 grmb of a mixture of 8 vols of H₂SO₄ and 2 vols Aq, and heating till

gas bubbles begin to rise A violent reaction occurs, heat being again applied when this subsides, until no further reaction takes place The acid partly crystallises out, and is partly extracted with ether (W Slædel, B 19, 1949)

Properties -Thin laminæ, sl sol cold water,

v. sol hot water, alcohol, and ether.

Reactions—1 Yields benzoic aldehyde, formic acid, and CO₂ when oxidised by chromic acid mixture—2 HNO, yields o- and p- nitro acids (Pirogoff, B 5, 332)—3 Electrolysis of a dilute solution gives benzoic aldehyde and benzoic acid and two neutral substances [93°] and [115°] (Slawik, B 7, 1051) -4 Ozonised oxygen yields PhCH₂CO O CH₂Ph (818°) -5 When administered to animals it appears in the urine as phenyl aceturic acid, and increases the amount of urea (Salkowski, B 12, 653, H 12, 222) -6 Phthalic anhydride and HOAc form benz ylidene phthalide on heating Tetra chlorophthalic anhydride (40 pts), phenyl acetic acid (20 pts), and NaOAc (1 pt) form, in like manner, OHPh C₂O₂, C₄Cl₄, melting above 360°, whence NaOH forms CH_Ph CO C₄Cl₄ CO₂H [175°] (Ga briel, B 20, 2869) Di-chloro phthalic anhy dride forms the corresponding compound CHPh C₂O₂ C₆H₂Cl₂ [210°], whence alkalis yield C1.H1.Cl2O. [117°] -7 HIAq and P at 200° form C_aH₁₁PO₂ [136^c], which crystallises from water in needles, and gives CaA" 2aq, BaA" 2aq, and Ag₂A" (Guye, J 1884, 468)

Salts — CaA', 2aq — CaA', 2aq — BaA', 2aq
v sol water — PbA', aq — AgA' small laminæ
Methyl ether MeA' [220°] S G 12 1 044
Liquid (Radziszewski, Z [2] 5, 358)
Ethyl ether EtA' (229° cor) S G 12

1 086 Converted by heating with sodium into acetic ether, sodium phenyl acetate, a solid C₂₄H₁₈O₂ [175°] (? tri phenyl-phloroglucin), and an oil (? CH₂Ph CO CHPh CO₂Et) (Hodgkinson,

C J 37, 481, C J Proc 2, 189)
Amido ethyl ether Cl CH₂(NH₂) CH₂A' Formed from C2H4Br NH CO CH2Ph and hot

water (Eifeldt, B 24, 3222) — B C, H, N,O, [138°]
n Propyl ether PrA' (238° cor) S G

18 1 0142 Made by heating alcoholic potassium phenyl acetate with PrI for two days Sodium acts on it, forming propyl acetate, sodium phenyl-acetate, a yellow oil $C_{22}H_{20}O_{2}$, (335° at 50 mm), and a small quantity of a solid, $C_{10}H_{24}O_{3}$, forming white needles (from petroleum), [170°], S G 17 1 039 This solid is also formed by the action of sodium on the oil C22H20O2, as well as on the corresponding oil $C_{18}H_{16}O_2$ formed from ethyl phenyl-acetate The solid forms an acetyl ethyl phenyl-acetate derivative [100°] (Hodgkinson, C J 37, 483)

Iso-butyl ether (CH₂)₂CH CH₂A' (147°

Sodium gives isobutyl acetate and ali oil cor)

(Hodgkinson, C J 37, 485)

Bensyl ether PhCH₂A'
(270° at 160 mm) S G ¹¹ 1 094 (318°) (S), Got by heating benzyl chloride with alcoholic potassium phenylacetate for a week (H) Heated with sodium it forms sodium phenyl acetate, the salt of an acid $C_{11}H_{14}O_{22}$ [120], possibly $\alpha.\beta.d_{11}$ phenyl-propionic acid, and an oil, $C_{22}H_{24}O_{2}$ (820° at 60 mm), possibly the benzyl ether of that

Chloride CH.Ph COCl (108° at 17 mm.). S G 29 1 1682 (Anschütz a Berns, B 20, 1389;

Hinsberg, B 23, 2962).

Anhydride (CH2Ph CO)2O [725°] Formed [from the chloride and the Ag salt (A a B)

Amide CH,Ph CO NH, (288°) [158°] Formed from the nitrile by heating with alcoholic KSH (Weddige, J pr [2] 7, 99) Formed also by heating phenylacetamidine hydrochloride with oxala jetic ether and dilute (10 pc) NaOHAq (Pinner, B 22, 1627), and by the action of yellow ammonium sulphide on acetophenone (Willgerodt, B 21, 534) Plates, v sol hot water Forms with HgO a compound crystallising in needles [208°] (Reimer, B 13, 741) K3rO and HOAc give CH,Ph CO NHBr [12_o], crystallising from benzene in needles, and yielding benzylamine on warming with potash (Hoogewerff a Van Dorp, R T C 6, 385) Aldehyde and a few drops conc HClAq give (C.H. CH, CO NH), CHMe [228°] Chloral gives an analogous body

Diethylamide CH2Ph CO NEt (296° uncor) Formed from the chloride and diethylamine in ether (Hausknecht, B 22, 324)

Bromo-ethyl amide CH₂Ph_CO NH C₂H₄Br [85°] Plates

β Bromo propyl amide CH₂Ph CO NH CH₂.CHMeBr [46°] Formed from the chloride and C₂H₂Br(NH₂) Needles

γ Bromo propyl-amine CH₂Ph CO NH CH₂CH₂CH₂Br [44°] Needles, converted by KOH into CH₂CH₂O CH₂Ph (Elfeldt, B 24, 3224)

Antitude CH2Ph CO NHPh [117°] (Hofmann, B 13, 1225) Got, by intramolecular change, by the action of PCl₃ on the oxim of deoxybenzoin (Gunther, A 252, 71)

Di-phenyl amide CH,Ph CO NPh, [72°] Satiny needles (from ether) (Hausknecht) Phenyl hydraside C14H1, N2O [167°]

White flakes (Bulow, A 236, 196)

Netrele C.H. CH. CN Benzyl cyanide (232° cor) S G 12 1 015 H C 1,023,000 H F -27,900 (Berthelot a Petit, C R 108, 1219) The chief constituent of the oils of garden cress (Lepidium sativum) and of nasturtium (Tropwolum majus) (Hofmann, B 7, 1293) Formed by boiling benzyl chloride with alcoholic KCy (Cannizzaro, A Ch [3] 45, 468) Preparation -By digesting benzyl chloride (1 kilo), crude KCy (1 kilo), and dilute alcohol for a week Tribenzylamine remains in the retort after distilling off the benzyl cyanide below 300° Reactions —1 A specimen (200°-230°) treated with ZnEt, the temperature being kept below 130°, formed a product which, when decomposed by alcohol, gave cyanbenzine (C₂H₂N)_n and benzacin, C₃₂H₂N₂O, an indifferent body [150°] -2 Reduced by sinc and HClAq to C.H. CH. CH. NH, (Bernthsen, B 8, 691) —3 Alcoholoammonium sulphide forms C₄H₄ CH₂CS NH₂ [98°] — 4 Water at 250° forms the amide, ammonium acetate acts in like manner (Bernthsen, B 9, 429) —5 Bromine forms C.H., CHBr CN and very sparingly soluble C.H. CHBr CBr(NH) [c 200°], which is crystalline, is decomposed by hot water and alcohol, and yields mandelic acid when heated with dilute HCl at 150° (Reimer, B 14, 1797) —6 Pyruvic acid and H.SO, in the cold form C₁₈H_nN₁O₄ [1457] (Böttinger, B 14, 1600).

Paranitrile (C₂H₁N)_n n=8? Cyanbensine.

[1717] (F 'a T), [221°] (P.) Obtained by ex-

tracting with alcohol the product of the action of ZnEt, on the isomeric nitrile (Frankland a Tompkins, C J 37, 568) Occurs in small quantity in the product of the action of alcoholic KCy on benzyl chloride (Pinner, B 17, 2010) Silky needles Hardly sol alcohol, sol. CS2, and glacial acetic acid Forms a gummy mass with warm dilute HCl, possibly a salt

Di-phenyl-acetic acid C1. H12O2 te CHPh, CO,H Deoxybenzilic acid Mol w Formed by reducing benzilic acid [148°] with HIAq (Jena, A 155, 84) and by heating CHPhBr CO.H (1 mol.) with benzene (1 mol.) and zinc dust (Symons a Zincke, B 6, 1188, A 171, 122) Obtained also by saponifying its nitrile or amide Needles (from water), sl sol cold water, v sol alcohol and ether Yields benzophenone on oxidation, and di phenyl methane on distillation with soda lime Bromine forms CPh₂Br CO₂H

Salts —BaA', 2aq Efflorescent monoclinic crystals —CaA', 2aq —AgA' amorphous pp Methyl ether MeA' [60°] Plates (from

Prisms

alcohol) (Rattner, B 21, 1316) Ethylether EtA' [58°] Amide CHPh, CONH, [58°] Fin [166°] Got by action of KOH (6 g) in alcohol on the nitiile (2 g) (Anschutz'a Romig, A 233, 347), and by heating the ammonium salt under pressure at 230° (Neure, A 250, 141) Plates (from alcohol)
Nitrile CHPh.CN [76°] (N), [73°]

(N), [73°] (Fa S) (183° at 12 mm) Formed by heating CHPh₂Br with HgCy₂ for 18 hours at 165°, and extracting with benzene (Friedel a Balsohn, Bl [2] 33, 589) and by heating the acid with lead sulphocyanide at 170° (Freund a Immerwahr, B 23, 2845) Got also, together with a polymeride [168°], by nitrating diphenyl ethane and reducing the resulting C₁₄H₁₀N₂O₄ [148°] with SnCl₂ and alcoholic HCl (A a. R), and by treating the amide with PCl, in POCl₂ (N) White needles (from ligroin and Alcoholic NaOEt and benzyl chloride form CPh₂(CH₂Ph) CN [126°] An ethereal solution of iodine (1 mol) gradually added to an alcoholic solution of the nitrile (2 mols) and NaOEt (1 mol) forms CN CPh. CPh. CN [c

Tri-phenyl acetic acid CPh, CO2H [264°] Formed by the action of fuming HClAq and HOAc on the nitrile at 200° (E a O Fischer, B 11, 1598, A 194, 242) Prepared by heating CCl, CO₂H (250 g), benzene (340 g), and AlCl₃ (250 g), mixing the product with water and dis tilling with steam, the residue of aluminium triphenylacetate is decomposed by NH, Aq and the filtrate ppd by HCl, the yield being 5 pc (Elbs a Tölle, J pr [2] 32, 624) In this preparation two by products (C.H.O), [825°] and (C₁₂H₂O)_n [75°] crystallising in yellow needleg are also formed Monoclinic prisms (from alcohol), sl sol HOAc Very feeble acid The NH4 salt gives off NH, spontaneously The K salt, ppd as needles by conc KOHAq, is decomposed by water Fuming H.SO, at 100° forms SO,H C,H, CPh, CO,H, which yields BaA'aq, an amorphous salt -Salt AgA' Powder, not affected by light

Natrale CPh. (N [1275°] Formed from HgOy, and CPh. Cl at 160° and from KCy and CPh.Br (Elbs, B 17, 700) Monoclinic prisms (from ligroin or HOAc) Converted by alcoholic potash into a polymeride [210°] crystallising in colourless needles

References - Amido-, Bromo-, Bromo amido, Bromo NITRO-, CHLORO, IODO-, and OXY PHENYL-ACETIC ACID

PHENYL-ACETIC ALDEHYDE C,H,O 16 C.H. CH2.CHO. (206°) (Radziszewsky, B 9,

872), (194°) (Etard) Formation -1 By distilling calcium phenylacetate with calcium formate (Cannizzaro, A 119,254) —2 From α bromo- (or chloro) β oxyphenyl-propionic acid CHPh(OH) CHBr CO.H by distilling with dilute Na2CO, the yield being 75 pc (Lipp B 16, 1286, Erlenmeyer, A 219, 179)—8 By boiling PhCH(OH) CH₂OH (1 pt) for an hour with H₂SO₄ (3 pts) and water (12 pts) (Zincke, A 216, 301) Stronger H₂SO₄ yields C₁₆H₁₂ [101°] —4 From ethyl benzene by successive treatment with CrO_2Cl_2 and water (Etard, A Ch [5] 22, 248) -5 By distilling phenyl glycidic acid with dilute H₂SO, (Erlenmeyer, B 13, 304).

Properties -Oil Forms a crystalline com-

pound with NaHSO₃
Reactions—1 With acetoacetic ether and NH_a it yields benzyl-di-methyl pyridine di carboxylic ether dihydride C₃H₂N(C₂H₂)Me₂(CO₂Et)₂ [1 3 5 2 6] [115°] (Jeaurenaud, B 21, 1784) -2 HCy forms CH₂Ph CH(OH) CN [58°], S 1 at 15°, crystallising in stellate groups of colourless needles, v sol alcohol.—3 HNO₃ (S G 149) at —12° give o and p-nitro benzoic aldehyde

Phenyl-hydraside CH,Ph CH N,HPh [58°] Prisms, v sol alcohol Converted into phenyl indole by heating with ZnCl_2 at 180° (Fischer a Schmitt, B 21, 1072)

Ethyl derivative C,H, CH CH OEt (217°) SG $^{\circ}$ 981 Formed from ω chlorostyrene and alcoholic potash (Erlenmeyer, B14, 1868) Oil, easily decomposed by heating with water into alcohol and the aldehyde

Di-phenyl-acetic aldehyde CHPh, CHO (315°) Formed by heating hydrobenzoin (1 pt) or isohydrobenzoin with (6 pts of) dilute (20 pc) H₂SO, for 8 hours at 210° (Zincke a Breuer, B 9, 1769, A 198, 182, Weise, A 248, 38) Oil, v sol alcohol and ether Yields benzo Yields benzophenone and CO, on oxidation Forms a crys talline compound with KHSO. Alcoholic potash yields di phenyl-carbinol and di-phenyl methane Nascent HOy yields CHPh. CH(OH) CN, upon which alcoholic hydrogen chloride reacts with formation of CHPh2 CH(OH) C(NH2Cl) OEt [185°] The aldehyde appears to form condensation products [168°] and [214°] on standing

Phenyl hydraside CHPh2 CH N2HPh Flat stellate needles (from hot alcohol), v sol ether (Rudolph, A 248, 101)

Oxim CHPh, CH NOH [120°] White needles, formed together with another body [145°] by the action of hydroxylamine in dilute alcohol (Auwers, B 24, 1780)

PHENYL-ACETIC CARBOXYLIC ACID v. CARBOXY-PHENYL-ACETIC ACID

PHENYL-ACET-IMIDO-ACETATE

C.H. CH. C(NH) OAc [129°] White needles V e sol. alcohol, al sol cold water Formed by boiling phenyl acet-imido etayl ether with Ac.O (Luckenbach, B. 17, 1493)

PHENYL-ACETIMIDAMIDE v ACETAMIDINE

PHENYL-ACET-IMIDO-ETHYL ETHER

C.H. CH, C(NH) OEt The hydrochloride B'HCl [c 85°] is formed by passing dry HCl into a solution of phenyl-acetonitrile in absolute alcohol (Luckenbach, B 17, 1421) The fire base is a colourless liquid of aromatic odour, decomposed on distillation into alcohol and phenyl aceto nitrile The hydrochloride is resolved on fusion into phenyl acetamide and EtCl

PHENYL-ACETONITRILE v Nitrile of

PHENYL ACETIC ACID

PHENYL ACETONYL SULPHIDE C.H. SO i.e PhS CH, CO CH, [35°] (144° at 15 mm) Formed from chloro acetone and NaSPh (Delisle, B 22, 308) Large tables (from ether), turned dark violet by hot H2SO. Yields a phenylhydrazide [83°]

The corresponding sulphone Ph SO₂ CH₂Ac [58°] is formed from chloro acetone and sodium benzene sulphinate (R. Otto, B 19, 1642)

PHENYL ACETOPHENONE

[1 3]C₆H₅ C₆H₄ CO CH₅ [121°] (c 326°) Formed from diphenyl, AcCl, and AlCl₅ (Adam, A Ch [6] 15, 255) Prisms, reduced by sodium amalgam to the carbinol [86°]

DI PHENYL ACETOXIM (so called) v Oxim

of Benzophenone

PHENYL-ACETURIC ACID

CH₂Ph CO NH CH₂CO₂H [142°] S 73 at 12° Occurs in horses' urine, and is also found in urine after a dose of phenyl acetic acid (Sal kowski, B 17, 3010, H 7, 162) Formed by the action of the chloride or anhydride of phenyl acetic acid on glycocoll (Hotter, B 20, 81, J pr [2] 38, 98) Small trimetric crystals (from alco |2| 00, 90| Small trimetric crystals (from alco hol), a b c = 890 12374 V sl sol ether, v sol hot water and alcohol—CaA'₂ 2aq S 316 at 112°—CuA'₂ aq—PbA'₂ aq prisms—ZnA'₂ plates, v sol hot water—AgA' amorphous

Methyl ether MeA' [86°] Needles

Ethyl ether EtA' [79°] Prisms

Propyl ether PrA' [31°] Plates

Amida CH Ph CONH CH CONN

Propyl ether PrA' [31°] Plates Amide CH,Ph CO NH CH, CONH, [174°]

Pearly hexagonal plates, v sol hot water With

HgO it yields Hg(C₁₀H₁₁N₂O₂)₂
PHENYL-ACETYL ACETONE C₁₁H₁₂O₂ i.e. C.H. CH. CO CH. CO CH. Benzyl methyl methylene di-ketone (266°-269° at 748 mm) Has weak acid properties

Formation -Phenyl acetyl acetoacetic ether, formed by the action of phenyl acetyl chloride upon sodio aceto-acetic ether, is boiled with

water for 6 hours

Properties —Colourless oil Sol alcohol. ether, benzene, hot water, strong acids, and di-With planyllute alkalis, sl sol cold water hydrazine it condenses to phenyl benzyl methyl pyrazole

Salts — A'Ag white pp — A'Na× crystalline solid (Fischer a Bulow, B 18, 2136

PHENYL-ACETYLENE O.H., t.e C.H., C.C.H. Acetenyl benzene (141 6° cor) S G 3° 9295 μ.= 1 542 (Brühl, Α 285, 13) S V 125 8

Formation -1 By distilling phenyl propiolic acid with dry Ba(OH), (Weger, A 221, 70) —
2 By boiling styrene dibromide with alcoholic potash, and heating the resulting bromo styrene with alcoholic potash (Glaser, Z [2] 5, 97, A 154, 155, Hollemann, B. 20, 8080).-8 From acetophenone by treatment with PCls, the resulting C₆H₅ COl₂ CH₃ being heated with conc alcoholic potash at 120° (Friedel, Z [2] 5, 123) 4 By the passage through a red hot tube of a mixture of styrene and hydrogen, or of benzene and ethylene (Berthelot, C R 67, 952)

Properts - Liquid with peculiar odour Its accoholic solution forms a yellow pp Cu2(C8H3)2O with ammoniacal cuprous chloride and a white pp Ag₄(C₈H₅)₂O with ammoniacal AgNO₃ These pps are explosive Sodium added to its ethereal solution ppts CPh CNa as a white powder, which takes fire in the an, and is reconverted by water

into phenyl-acetylene

Reactions -1 Unites with bromine -2 Sodium and CO2 give sodium phenyl propiolate, (Paternò, G 2, 553) —3 Sodrum and EtI give PhC CEt (202°) (Morgan, C J 29, 162) —4 H SO,, followed by water, yields acetophenone (Friedel a Balsohn, Bl [2] 35, 54) —5 Boiling HOAc and zinc dust reduce it to styrene (Aron

stein a Hollemann, B 22, 1181)

Di phenyl acetylene C₁₄H₁₀ ie CPh CPh lane [71°] (Béhal) Formed by boiling [71°] (Béhal) Tolane CPhHBr CPhHBr or the corresponding di chloro di phenyl ethane, with alcoholic potash (Lim pricht a Schwanert, A 145, 347, Fittig, A 168, 74) Formed also by the action of sodium amal gam on an alcoholic solution of CPhCl2CPhCl2 (Li bermann a Homeyer, B 12, 1974) Large ciystals (from ether) May be distilled Yields di phenyl ethylene (stilbene) when heated with HIAq and P at 180° (Barbier, J 1876, 366) Conc H2SO Yields benzoic acid on oxidation gives a green colour, and on warming to 60° diluting with water and distilling with steam, phenyl benzyl ketone (deoxybenzoin) [55°] 18 produced (Béhal, Bl [2] 49, 337)

Chlorides 1 DI CHLORO DI PHENYL ETHYL ENE and TETRA CHLORO DI PHENYL-ETHANE

Dibromide v DI BROMO DI PHENYL ETHYL-

Di phenyl di acetylene C16H10 16

CPh C C CPh [97°] (G), [88°] (H) Formed by shaking the cuprous compound of phenylacetylene with alcoholic NH, and air, or, better, with alkaline K₂FeCy₆ (Glaser, A 154, 159, Baeyer a Landsberg, B 15, 57) Long needles (from dilute alcohol), v sol ether Hot H.SO. carbonises it In ethereal solution Br forms $C_{16}H_{10}Br_{4}[178^{\circ}]$ and $C_{22}H_{20}Br_{6}[149^{\circ}-153^{\circ}]$ (Holle mann, B 20, 3081)

Picric acid compound CieHioCeHiNO, [108°] Yellow crystals (from alcohol)

NITRO-References - Amido, Iodo, and PHENIL-ACETYLENE

TRI PHENYL ACETYLENE-TRIAMINE

 $\mathbf{C}_{20}\mathbf{H}_{1}$, \mathbf{N}_{2} to $\mathbf{N}_{3}\mathbf{H}_{2}(\mathbf{C}_{2}\mathbf{H}_{2})\mathbf{Ph}_{3}$ [190°] Formed from acetylene tetrabromide, aniline, and alco holic potash (Sabanejeff, A 178, 125) Needles. v sl sol cold alcohol —Salts B'2H2PtCl3 — B'4H4Hg3Cl10 amorphous pp DI-PHENYL ACETYLENE - DI-THIO-DI-

UREA CS

NH CPh NH CS Formed from benzil and thio urea at 145° (Anschutz a Geldermann, A 261, 134) Crystals, decomposing at 300°, v sl sol alcohol

LI-PHENYL-ACETYLENE-DI-URBA

CO NH CPh NH CO Tolane-urea Formed

by heating benzil with urea at 175° (Anschutz a Geldermann, A 261, 183, Angeli, B 24, 606, G 19, 563) Crystals, not decomposed at 315°, v sl sol alcohol and ether Reduces ammoniacal AgNO,

Dr acetyl derivative C₁₈H₁₂Ac₂N₄O₂ [266°

PHENYL-ACETYL-SUCCINIC ACID ACETYL-PHENYL SUCCINIC ACID The mono ethyl ether of this acid yields on treatment with alco holic NH, a compound $C_{12}H_{12}N_2O_2$ [264°], which forms, on saponification, a compound $C_{12}H_{11}NO_3$ [148°], crystallising in small needles (Weltner, B 18, 793)

PHENYL ACRIDINE C10H13N 1 e

 $C_eH_4 < \stackrel{CPh}{\sim} C_eH_4$ [181°] (c 404°) 129 7 [H = 1]

Formation — (Bernthsen, B 15, 3011, 16, 1809, 19, 425, 20, 1552, A 192, 19, 224, 12) 1 By heating benzoyl diphenylamine (30 g) with ZnCl (30 g) at 210°-280° -2 benzotrichloride, diphenylamine, and ZnCl2 -3 By heating benzonitrile with diphenylamine hydrochloride at 240°—4 By heating di phenyl benzamidine hydrochloride to 250°-5 In small quantity by heating di phenyl amine with cinnamic acid and ZnCl2.-6 By diazotising chrysaniline (di amido phenyl acridine) and boiling the product with alcohol (Fischer a Körner, B 17, 206, A 226, 184)

Preparation —By heating benzoic acid (50 g) diphenylamine (70 g) and ZnCl₂ (150 g) at 260° The yield of crude base (50 g) is for 10 hours

Properties - Colourless thin prisms (from alcohol), thick yellowish prisms (containing C, H, or tables (from benzene) V sol benzene m sol ether, sl sol alcohol, insol water Solu tions of its salts exhibit green fluorescence Not affected by boiling dilute HNOs, by fuming HCl at 260°, by AcCl, by AcO at 190°, by Bz₂O at 160°, by potash fusion, by heating with H₂SO₄ (3 vols) diluted with water (1 vol), or by distillation with soda lime

Reactions -1 CrO, in HOAc gives benzoic acid and CO .- 2 On oxidation with KMnO, it gives phenyl quinoline carboxylic acid the other hand, its alkyl halogen addition pro ducts give rise to phenyl amido benzoic acid $C_gH_4(NHPh)CO_2H$ on oxidation with KMnO₄ (Claus a Nicolaysen, B 18, 2706) -3 Yields on nitiation with H2SO4 and fuming HNO, di nitro phenyl-acridine C19H11(NO2)2N, which is sol aqueous or alcoholic HCl but sl sol al cohol, and tri nitro phenyl acridine, which crystallises from toluene and alcohol in minute yellow needles, hardly sol alcoholic HCl, and converted by hot SnCl into a red dye (? triamido-phenyl acridine), which becomes colour less on further reduction

Salts —Partially decomposed by water — B'HCl orange needles or prisms, sl sol cold water, sol alcohol Its solution exhibits darkgreen fluorescence — B'HCl 3aq red crystals — B'₂H₂PtCl₈ — Nitrate [188°] Yellov — B'_H_PtCl, — Nitrate [188°] Yellow needles, sl sol HNO, —Sulphate yellowish. red trimetric crystals, v sol hot water —Pi-Hair-like crystals (from alcohol) crate Phenyl-acridine does not appear to form an acetate

Methylo-chlorede B'MeCl soluble | needles -B'2Me2PtCl, decomposes below 70°

Methylo-netrate B'MeNO. Sparingly

sol yellow needles

Methylo-todide B'Mel. Black monoclinic prisms (from alcohol), insol. ether Converted by KOHAq, by NH, Aq, or by moist Ag, O, into B'MeOH [1080], which is also got by oxidising CeH. CHPh CeH., a body to which it is re

duced by tin and HClAq

Hydrede C.H. CHPh C.H. [164°]

Formed by reducing phenyl-acridine hydrochloride in aqueous solution with zinc-dust or by adding sodium amalgam to an alcoholic solu-Colourless needles, with no basic pro perties, sol alcohol and ether Alcoholic AgNOs oxidises it to phenyl acridine, a change which is slowly effected even by air. It yields an acetyl derivative C₁₈H, Acn [128°], and is converted by MeI at 140° into C₁₈H, MeN [104°], whence HCl and NaNO2 produce the methylo hydroxide of phenyl-acridine (v supra)

Dissulphonic acid Got by heating phenyl acridine (10 g), H_2SQ_4 (15 g), and $H_2S_2O_7$ (15 g) for 12 hours at 150° Its dilute solutions exhibit green fluorescence The salt C₁₉H₁₁N(SO₂Na)₂ is insol absolute alcohol, and in very dilute solutions exhibits blue fluorescence The Ba and mercurous salts are nearly insol Aq

References -- Amidoand Oxy-PHENYL-

ACRIDINE

PHENYL-ACRIDINE CARBOXYLIC ACID $C_{\bullet}H_{\bullet} < N \longrightarrow C_{\bullet}H_{\bullet}$ Acridyl-benzoic acid Formed by heating phthalic anhydride (30 g) with diphenylamine (45 g) and ZnCl, (75 g) for 12 hours at 190° (Bernthsen a Traube, B 17, 1510, A 224, 45) Yellow crystalline powder, sol acids and alkalis, insol water, sl sol boiling alcohol Its solutions in dilute acids have a green fluorescence, in alkalis a blue fluorescence Split up by heat into CO₂ Yields a hydride [160°and phenyl-acridine

Salts —NaA'aq colourless pearly plates or long needles —HA'HCl. [163°] Yellow crystals (from hot dilute HCl), al sol hot water colourless pearly plates

An isomeric acid C.H. CPh C.H. CO.H. [252°-255°], formed by oxidation of phenylmethyl-acridine with chromic acid mixture, is sl sol alcohol, and gives sparingly soluble BaA'2 (Bonna, A 239, 62)

PHENYL-ACRYLIC ACID v CINNAMIC ACID and Atropic Acto

Di-phenyl-acrylic acid v PHENYL-CINNAMIO

PHENYL-ALANINE v a-Amido Phenyl-PROPIONIC ACID and PHENYL-AMIDO PROPIONIC

PHENYL ALDEHYDE v PHENYL-ACETIC ALDEHYDE

PHENYL ALDEHYDO-BENZYL KETONE Ph.CO CHPh CHO [110°]. Formed from deoxybenzoin, formic ether, and NaOEt in ether (Claisen a Meyerowitz, B 22, 8279) Yellowishwhite crystals. FeCl, gives a dark violet colour PHENYL ALDEHYDO-FIHYL KETONE

PhCO.CHMe.CHO [119°] Formed from

phenyl ethyl ketone, formic ether, and NaOEt in Et₂O (Claisen a Meyerowitz, B 22, 3276) White needles, v sol alcohol and water FeCl, colours its alcoholic solution dark violet Gives

an anilide [182°] crystallising in needles PHENYL ALDEHYDO-PROPYL KETONL Ph CO CHEt CHO [87°] Formed 'rom phenyl n-propyl ketone, formic ether, and NaÔEt in ether (Claisen a Meyerowitz, B 22, 3278) White plates FeCl, gives a dark-violet colour The anilide [120°] crystallises in white needles

TETRA-PHENYL-ALDINE v TETRA PHE? YI -

PYRAZINE

PHENYL-ALLENYL-AMIDOXIM v NAMIDOXIM

PHENYL-ALLOPHANIC ACID ether C.H.NH CO NH CO.Et [120°] Formed from phenyl-urea and chloro-glyoxylic ether COCl CO₂Et (Stojentin, *J pr* [2] 32, 18) Needles, v sol alkalis and cone HClAq

Phenylether NHPh CO NH CO,Ph Formed from phenol and cyanic acid vapour (Tuttle, J 1857, 451) Crystals (from alcohol), insol cold water Decomposes at 150° into phenol and cyanuric acid

Bensyl ether NHPh CO NH CO₂C H, [158°] Formed by heating phenyl cyanate with benzyl carbamate at 150° under pressure (Traube, B 22, 1574) V sl sol water, m sol alcohol

D1-phenyl-allophanic acid NHPh CO NPh CO2H

Methyl ether MeA'

[231°]
[GRO] Formed from Ethyl ether EtA' [58°] di-phenyl di isocyanate Ph₂N₂C₂O₂ and alcohol (Hofmann, B 4, 246), and by the action of HgO and alcoholic NH, on NHPh CS NPh CO Et (Seidel, J pr [2] 32, 266) Needles, sl sol ether Yields (C₁₆H₁₆N₂O₃)₂3HgO [129°], crystallising in prisms (from alcohol)

Isoamyl ether C,H,A' [58°] Reference - DI-BROMO DI PHENYL ALLOPHANIO

PHENYL ALLYL-BENZYL KETONE

C_cH₃ CO CHPh C_sH₃ (337°) Formed from de oxybenzoïn, NaOEt, and allyl 10d1de (Buddeberg, B 23, 2067) Oil, v sol alcohol

PHENYL ALLYL CYANAMIDE C, H, N, 1 & C.H.N C NC.H. Carboallylphenylimide [105°] Formed from phenyl allyl thio-urea and Pb(OH). (Bizio, J 1861, 497) Silky needles (from dulute alcohol) —B'HgCl₂ amorphous —B'₂H₂PtCl₅ PHENYL-ALLYLENE C₅H₅ C C CH₅ (185°)

Formed by the action of alcoholic potash on the bromo-propenyl-benzene, which is got by boiling CHPhBr CMe CO₂H with water (Körner, B 21, Yellowish liquid, with unpleasant odour Yields a liquid dibromide (c 258°) and a solid tetrabromide [75°] Aqueous HgCl₂ forms white amorphous (C₀H₂)₂Hg₂Cl₂O₂, which on heating with HCl yields phenyl ethyl ketone

u-PHENYL-ALLYL-HYDRAZINE

C₈H₅ NPh NH₂ (198° at 184 mm) Formed by reducing the nitrosamine derived from allylaniline (Michaelis a Claessen, B 22, 2233) also from allyl-bromide and phenyl hydrazine. Oil, v sol dilute HCl Reduces Fehling's solution on warming Oxidised by aqueous FeCl, to the tetrazone C,H,NPh N N NPh C,H, [86°]. Benzoic aldehyde yields C,H,NPh N C,IPh [52°]—B'HCl [187°] Silky needles

Bensoyl derivative C.H., AcN. [139°]

s-Phenyl allyl-hydrazine $C_9H_{12}N_2$ i ePh NH NH C₂H₄ (172° at 60 mm) Got from phenyl-hydrazine and allyl bromide (Fischer a. Knoevenagel, A 239, 203) Oil, sol dilute acids Reduces cold Fehling's solution Oxies by HgO to benzene-azo propylene .N.C.H., an oil, (95°-100° at 27 mm) DI-PHENYL-DI-ALLYLIDENE-DIAMINE dises

C₁₈H₁₈N₂ s.e. N₂Ph₂(C₃H₄)₂. Formed from annline and acrolein below 0° (Schiff, A Suppl 3, 358)

Yellow resin —B',H.PtCl, DI-PHENYL-DI-ALLYLIDENE-ETHYLENE DIAMINE C2H4(N CH CH CH C6H5)2 Formed by mixing ethylene-diamine (1 mol) with cinnamic aldehyde (2 mols) (Mason, B 20, 271) Large colourless tables (from ether) sol alcohol and benzene, m sol ether composed into its constituents by acids

PHENYL ALLYL OXIDE C.H. O C.H (194°) Formed from allyl bromide and NaOPh

(Henry, B 5, 455) Liquid

PHENYL ALLYL SULPHIDE C.H. S.C.H. 208°) Formed by distilling the acid CH₂ C(SPh) CH₂ CO₂H (Escales a Baumann, B 19, 1792) Liquid, forming a blue solution in

PHENYL - ALLYL - THIOSEMICARBAZIDE C_eH_sNH NH CS NHC_sH_s [119°] Formed from phenyl hydrazine and allyl thiocarbimide dis solved in benzene (A E Dixon, C J 57, 263, Avenarius, B 24, 268) Silvery needles, insol water, v sol alcohol and ether Gives a mahogany colour with FeCl₃
Di phenyl-allyl thiosemicarbazide

C₆H₅N(C₂H₅) NH CS NHPh [103°] from phenyl allyl-hydrazine and phenyl thio carbimide (Michaelis a Claessen, B 22, 2237)

Needles (from hot alcohol)

PHENYL ALLYL THIO UREA C10H12N2S & 6 NHPh CS NHC, H, Phenyl throsmamine [98°] S (alcohol) 70 at 16° Formed by the action of aniline on oil of mustard (Zinin, A 84, 348) and of allylamine on phenyl thiocarbimide (Weith, B 8, 1529) Monoclinic crystals, insol water Cyanogen passed into its alcoholic solution forms C₁₂H₁₂N₄S, which crystallises from alcohol in stellate forms, and is converted by CS < N(C,H,) COdelute H2SO, into [161°], alcoholic sılver whence nıtrate forms $CO < \frac{N(C_6H_5)}{N(C_8H_5)} \frac{CO}{CO}$ [108°], which is resolved by baryta-water into oxalic acid and phenyl allylurea (Maly, Z [2] 5, 258)

PHENYL ALLYL THIO-UREA OXYLIC ACID v ALLYL-THIO URAMIDO-BENZOIC

PHENYL-ALLYL URBA NHPh CO NHC.H [97°] Formed as described under phenyl allylthio-urea Shining white needles

PHENYL-AMENYL-AMIDINE C, H, eN2 : 6 OMe, C(NH₂)(NPh) The oxalate B'H₂C₄O₄[192°] s formed by heating the corresponding valero-ntrile with aniline hydrochloride at 170° Freund a. Lenze, B 24, 2155)

PHENYL-AMIDO-ACETIC ACID C.H., NO. s.e. |H., (NHPh) CO.H. Phenyl glycocoll Antidocetic acid [127°] Formed by the action of aniline on bromo acetic acid and on chloroacetic acid (Michaelson a Lippmann, Z 1866,

15, Schwebel, B 10, 2046) Prepared by boiling aniline (45 g) dissolved in a little ether with chloro-acetic acid (25 g) and water (1500 cc) for half an hour, and rapidly evaporating to crystallisation (Rebuffat, G 17, 233) Byproducts are C₁₆H₁₁NO₄ [99°] (Meyer, B 14, 1325) and C₁₆H₁₆N₂O₂ [218°], which is perhaps CH₂(NHPh) CO NPh CH₂ CO₂H, though this formula may also be assigned to an isomeric acid [130°] formed by the action of alcoholic potash on di oxy-di-phenyl-pyrazine (Hausdörfer,

B 22, 1803, Abenius, J pr [2] 40, 432)

Properties—Small crystals, m sol water, insol ether By fusion with potash at 260° it yields a mass which forms indigo on oxidation (Heumann, B 23, 3043, cf Lederer, J pr [2] 42, 383, Biedermann a Lepetit, B 23, 3289)

Salt —CaA', 2aq Needles (from dilute alcohol), m sol hot water, insol alcohol On dis tillation with calcium formate it yields indole

(Mauthner a Suida, M 10, 251)

[48°] Formed by Methyl ether MeA' heating aniline with methyl chloro - acetate (Meyer, B 8, 1157) and by the action of aniline on methyl diazo acetate (Curtius, J pr [2] 38, 437) Rectangular plates (from ether) or needles (from alcohol)

Ethyl ether EtA' [59°] Formed in like manner Colourless plates (from ether)

Formyl derivative

[124°] NPh(CHO) CH, CO,H Formed saponification of its ether (2900-2950), which is the product of the action of chloro-acetic ether on sodium formanilde (Paal a Otten, B 23, 2593) Needles, v sol ether and hot water Yields C.H.NO.Na, a hygroscopic mass

Acetyl derivative NPhAc CH. CO.H [191°] Formed from phenyl amido acetic acid, Ac₂O, and benzene (R) Formed also by heating aniline with chloro acetic acid and NaOAc at 110°-150° (Hausdorfer, B 22, 1797), and by the action of boiling alcoholic potash on its ether (300°), which is got from sodium acetanilide and chloro-acetic ether (P a O) Pearly plates (from water) or needles (from HOAc-Ingroin), v sol alcohol and hot water Yields the salts NaA', BaA', 3aq, and CuA'

Chloro - acetyl derivative CH_CI CO NPh CH_ CO_H [133°] Formed from phenyl-amido acetic acid and chloro acetyl chloride (Abenius, J pr [2] 40, 429, 499) Plates or prisms, v sol alcohol On boiling with aqueous sodium carbonate it yields [128°], CH,(OH) CO NPh CH, CO,H crystallises in plates, forms the salts CaA' 6aq and BaA'_{2} , the anhydride $PhN < CO_{CH_{2}}CO > 0$ [169°], and the amide CH2(OH) CO NPh CH2 CONH2 [129°]

Plates, de-Bromo - acetyl derivative composing at 153° (Hausdörfer, B 22, 1803)

Benzoyl derivative CH2(NPhBz) CO.A.

[63°] Amorphous pp (Rebuffat) Netrosamene NPh(NO) CH_CO_H [105°] Yellow needles (Schwebel, B 11, 1132), v sol. warm water

Anhydride C.H.NO [268°] Got by heating the acid at 150° (Meyer, B 10, 1967). Needles (from alcohol), insol water.

Amide CH2(NHPh) CONH, [133°] Formed by heating chloro acetamide with aniline and NaOAc at 180° (Bischoff, B 22, 1809, cf Meyer, B 8, 1154) Minute needles (from water)

[112°] Antlide CH₂(NHPh) CO NHPh Formed by boiling chloro - acetic ether or CH,Cl CO NHPh with aniline (Wilm a Wischin, Z 1868, 74, Meyer, B 8, 1156, Hausdörfer, B 22, 1796) Formed also by heating aniline with alcohol and the compound of glyoxal with NaHSO_s (Hinsberg, B 21, 110) Needles (from alcohol), sl sol cold water

p - Tolurde CH₂(NHPh) CO NHC₄H₄Me [165°] Formed by heating aniline with fused NaOAc and CH2Cl CO NHC, H, Me at 150°

(Bischoff, B 23, 2000, cf Meyer, B 8, 1158) Netrele CH₂(NHPh) CN Formed from chloro acetonitrile and aniline in ether at 90° (Engler, B 6, 1004) Thick oil, forming a crystalline hydrochloride, decomposed by water

Reference - Bromo PHENYL AMIDO - ACETIC

Isomeride -Amido Phenyl Acetic Acid

Di-phenyl-di-amido-acetic acid C14H14N2O2 te CH(NHPh)₂ CO₂H Formed as a yellow crystalline powder by adding aniline to an aqueous solution of glyoxylic acid (Böttinger, B 11, 1559) Decomposed by hot water

∞-PHENYL AMIDO AČETOPHENONE

C₁₄H₁₅ON ve C₆H₅ CO CH₂ NHPh Aceto dhenone-amhde [93°] Prepared by the action of aniline on ω bromo acetophenone (Mohlau, B 14, 171, 15, 2467) Prisms or fine needles Sol alcohol, ether, chloroform, benzene, and On boiling with aniline it gives phenylindole Nitrous acid forms a nitrosamine C_cH_s CO CH₂ NPh(NO) [73°] —B'HCl prisms, decomposed by water —B'HBr

Acetyl derivative C16H15NO2 [127°] Bensoyl derivative [145°] PHENYL AMIDO-ACRIDINE

C₆H₄<\chr C CH C NHPh [176°] Formed by heating di-phenyl m phenylene diamine (5 g with ZnCl₂ (10 g) and formic acid (5 g of 90 pc) for 5 hours at 250° (Besthorn a Curtman, B 24, 2042) Flat brownish red needles, m sol alcohol, sl sol ether

PHÉNYL-AMIDO-ACRIDYL BENZOIC ACID

 $C_0H_4 < N$ $C_0C_0H_4$ CO_2H_1 C_1 C_2 C_3 C_4 C_4 C_4 C_4 C_4 C_5 C_6 C_6 -C CH C NHPh Formed by heating di phenyl m phenylene-diamine (5 g) with phthalic anhydride (10 g) at 250° (Besthorn a Curtman, B 24, 2047) Small red crystals, sol HOAc

PHENYL AMIDO-ACRYLIC ACID

CH(NHPh) CH CO₂H [194°] Formed from the product of the action of aniline on di bromosuccinic acid by boiling with potash (Reissert, B 20, 8105) Insol water, v sol alcohol -NaA' 21 aq sılky plates

Ethyl ether EtA' [144°]
PHENYL-AMIDO-AZOBENZENE v Benz-

ene-Azo-diphenylamine

DI PHENYL-AMIDO-BENZAMIDINE C₁₀H₁₇N₂ t.s C₆H₄(NH₂) C(NPh) NHPh Carbo triphenyltramine [198°] Prepared by heating p-nitro benzoic acid with aniline and POl, for two hours at 180° and reducing the product with an and HOl (Weith, B 12, 101) Formed also by the action of COL of The control of The contr by the action of COl, of CBr, and of COl, SO, Cl on aniline (Hofmann, Pr G, 284, Bolas a Groves, A. 160, 173, Michler a. Walder, B 14,

2174) Four-sided tables Split up by heating with HCl at 160° into aniline and p amidobenzoic acid Decomposed on distillation — B'HCl [282°] —B'₂H₂PtCl₈.

PHENYL-DIAMIDOBENZENE & AMIDO-

DIPHENYLAMINE

TRI-PHENYL-TRI-AMIDO-BEFZENE

C_sH_s(NHPh)_s [193°] Made by heating phloro-gluon with annine at 210° (Minunni, B 21, 1984) Needles (from alcohol) —B'HCl yellow powder, melting below 100°, decomposed by warm water —B',H,PtCl, [c 250°]

Tri acetyl derivative [173°] Needles. Tri bensoyl derivative [above 304°]

PHENYL AMIDO BENZOIC ACID

C₆H₄(NHPh)CO₂H [222° uncor] Formed by oxidation of the methylo-iodide of phenylacridine with MMnO4 (Claus a Nicolaysen, B 18, 2709) Small colourless needles ether and chloroform, insol water

Salts -A'Na 4aq easily soluble colourless plates — A'Ba 5aq small sparingly-soluble colourless plates — A'Ag*. very sparingly-solu small sparingly-soluble

ble white curdy pp

PHENYL AMIDO BENZYL KETONE

 C_6H_5 CO CH(NH₂) C_6H_5 [60°-70°] Formed by reducing the mono oxim of benzil with HCl and SnCl₂ (Braun, B 22, 556) and by heating desylphthalamic acid with HCl (Neumann, B 23, 996) White crystalline mass, becoming brown in air—B'HCl [210°] White needles—B'2H2PtCl₆ [193°]—Picrete B'C₆H₃N₅O₇

Carboxy-bensoyl derivative CaH, CO CHPh NH CO CaH, CO2H [168°] Got by warming desyl-phthalimide with NaOHAq -

AgC₂₂H₁₆NO₄ crystalline

Phenyl p amido benzyl ketone C₈H₃ CO CH₂ C₈H₄NH₂ [95°] S 33 at 100° Formed by reducing nitro benzil or nitro deoxybenzoin with tin and HCl (Golubeff, J R 6, 114, 11, 101, Bn 3, 109) Thin needles (from 114, 11, 101, Bn 3, 109) Thin needles (from dilute alcohol) —B'HCl Tables (from alcohol) S 25 in the cold —B'₂H₂PtCl₆ — B'₂H₂SO₄
Oxim C₆H₆ C(NOH) CH₂ C₆H₄NH₂ [141°]

Crystallises from alcohol (Ney, B 21, 2449)

PHENYL-a-AMIDO BUTYRIC ACID C.,H.,NO. ve CH, CH, CH(NHPh) CO.H [140°] Prepared by heating a bromo butyric acid with an ethereal solution of aniline at 100° (Duvillier, A Ch [5] 20, 205, Nastvogel, B Feebly acid —B'HCl —EtA' (278°) 22, 1792

Phenyl β amido-butyric acid [128°] CH₃ CH(NHPh) CH₂ CO₂H Formed by the action of baryts on the neutral isomeride (? betaine) which is obtained, together with the anilide, by boiling \$-chloro butyric ether with aniline (Balbiano, G 10, 144, B 13, 312) Tufts of needles, al sol water —BaA'₂ (dried at

100°) Scales B'HCl B'H,O,O [189°]

Antitae CHMe(NHPh) CH, CO NHPh The
hydrochloride BHCl [207°] crystallises in

colourless plates, sl sol hot water

Phenyl-a-amido-isobutyric acid CMe₂(NHPh) CO₂H [185°] Formed by saponification of the nitrile or the ether (Tiemann, B 15, 2042, Bischoff, B 24, 1044) Concentric

needles, m sol water May be sublimed

Ethyl ether Eth. [30°] (271°) Formed by heating aniline (2 mols) with brome iso-butyric soid (1 mol.). Thick prisms.

Amide UMe₂(NHPh) CONH₂ [137°]

Needles, sol alcohol and HClAq [94°]

Nitrile CMe2(NHPh) CN Made by heating acetone cyanhydrin with aniline Long

white prisms, sl sol hot water

Di phenyl di γ amido-butyric acid Nitrile [103°] CH(NHPh), CH, CH, CN Formed by heating CHO CH₂ CH₂ CN with aniline at 350° (Chautard, A Ch [6] 16, 185) Scales, sol water and alcohol

PHENYL AMIDO CHLORO v Chloro PHENYL AMIDO

PHENYL & AMIDO CINNAMIC ACID C.H. C(NHPh) CH CO.H

Methyl ether MeA' [93°] Formed from methyl benzoyl acetate and aniline (Knorr, A 245, 372) Prisms

Ethyl ether EtA' Formed in like manner (Conrad a Limpach, B 21, 521) Oil, v sol alcohol At 250° it yields (Py 1,3) oxy phenylquinoline and alcohol

 C_6H_5 C(NHPh) CH CO NHPh Anılıde [133°] Needles (from alcohol), almost insol Aq

PHENYL AMIDO CITRACONIC PHENYL

IMIDE? C(NHPh) CO NPh [160°] Formed by heating methyl oxalacetic ether with aniline at 180° (Wishcenus a Spiro, B 22, 3351) Golden plates, v sol hot alcohol

PHENYL AMIDO CRESOL C₁₃H₁₃NO (345°)NHPh C_bH_3 Me OH [1 3 5] [79°] Formed by heating orcin (1 pt), aniline (2 pts), and CaCl, (1 pt) at 260°-270° (Zega a Buch, J pr [2] 33, 538) Thick needles (from alcohol) Reduced by distilling over zinc dust to phenylm tolyl amine

Salt -B'HCl crystalline powder, decomposed by water

Isomeride OXY BENZYL ANILINE

PHENYL AMIDO CROTONIC ACID Methyl ether CH, C(NHPh) CH CO, Me [51°] Formed by mixing aniline with methyl acetoacetate (Conrad a Limpach, B 21, 1965) Prisms (from MeOH) Yields (Py 1,3) oxy methyl-quinoline when heated to 240°

Ethyl ether C_{1.}H₁₈NO, te CH₃ C(NHPh) CH CO₂Et Formed by allowing a mixture of aniline (1 mol) and acetoacetro ether (1 mol) to stand for some days in the cold, drying with K₂CO₃, and filtering (Knorr, B 20, 1397, cf Conrad a Limpach, B 20, 944, 22, 83) Strongly refracting oil, split up by acids and alkalis into its components At 200° it forms (Py 1,3) oxy methyl quinoline and a smaller quantity of oxy phenyl di methyl pyridine carboxylic ether

The anilide of acetoacetic acid (vol 1 p 19) CH, CO CH, CONHPh [85°], which is isomeric with phenyl-amido crotonic acid, is completely decomposed by heat, but yields the same oxy methyl quinoline on treatment with conc HClAq

PHENYL AMIDO 4 CUMYL KETONE C.H. CO C.HMe.(NH.) [5 1 3 4 6] Benzocumrde [180°] (c 360°) Formed by saponification of its phthalyl derivative (Froehlich, B 17, 1804, 2674) Long yellow needles or plates, v sol. alcohol and ether, not volatile with steam — B"H.PtCl. needles MeI forms orange C.H.Ce,Bz NMe,I [187°], crystallising from water in prisms (containing aq) ClCO Et gives

C_sHMe_sBz NH CO₂Et [105°], crystallising in needles

Acetyl derivative [170°] Needles Bensoyl derivative [227°]. Needles. Phthalyl derivative

C_eHMe₂Bz N<CO>C_eH, [181°] Formed by heating the phthalyl derivative of \$\psi\$ cumidine with BzCl and a little ZnCl2 at 180° Small rhombohedra, v sol hot water On saponifica tion by alcoholic potash it yields the acid C₀HMe₂Bz NH CO C₀H₄ CO₂H [195°], which crystallises in minute needles (containing aq)

PHENYL AMIDO-CYANURIC ACID v Cu anuric acid in the article Cyanic acid

PHENYL-AMIDO-ETHANE SULPHONIC ACID C₆H₅NH CH₂ CH₂ SO₂H Phenyl taurine [c 280°]

Formation -1 By heating the anilide with HCl -2 By heating chloro isethionic acid with an ethereal solution of aniline at 130° (Leymann, B 18, 871, James, C J 47, 369, J pr [2] 31, 415)—8 By the oxidation of phenyl thiohy dantoin with KClO, and HCl there is formed diphenyltaurocarbamic anhydride C15H14N SO3 [186°], which is split up by boiling baryta water into aniline, CO2, and phenyl taurine (Andreasch, M 4, 137)

Properties —Colourless leaflets, insol alcohol and ether, sol water forming an acid solution Aqueous cyanamide at 110° forms phenyltauro cyamine NH, C(NH) NPh C,H, SO,H, which crystallises from water in plates melting above

300° —BaA'₂ 3aq leaflets, m sol water Anılıde NHPh C₂H, SO,NHPh Formed, together with the anhydride CaH, NSO [69°], by the action of an ethereal solution of aniline (3 mols) on CH2Cl CH2SO2Cl (1 mol) -

HCl [169°] Colourless crystals DI-PHENYL-AMIDO-ETHYL AMIDO ACE-ACID NHPh CH₂ CH₂ NPh CH. CO₂H Formed from oxy di phenyl pyrazine hexahydride and alcoholic potash (Bischoff, B 23, 2026) Prisms, sol ether Converted into the parent substance by boiling with water or alcohol

PHENYL AMIDO-ETHYL KETONE

C₆H₂CO C₂H₄NH₂ Formed by the action of boiling HClAq on C₂H₄Bz N C₁O₂ C₆H₄ [85°], which is got from C₆H₅ CO C₂H₄Br and potas sium phthalimide (Schmidt, B 22, 3251)— B'HCl orystalline, v e sol water and alcohol

B',H,PtCl, -B'C,H,N,O, [160°] Needles
PHENYL-AMIDO-ETHYL-PHTHALIMIDE

C_aH₄ C₂O₂ N CH₂ CH₂ NHPh [100°] by heating bromo ethyl phthalimide with aniline at 150° (Gabriel, B 22, 2224) Lemon yellow needles, v sol dilute HClAq Converted by NaOHAq into CoH4(CO,H) CO NH.C2H4 NHPh [120°-130°], a crystalline powder

PHENYL-AMIDO-FUMARIC IMIDE

C(NHPh) CO NH? [202°] Formed by heating bromo-fumarimide with aniline (Löscher, B 21, 2718) Golden plates, sl sol. hot water

PHENYL-AMIDO-GLUTACONIC PHENYL-IMIDE C₁₇H₁₄N₂O₃ a.e C(NHPh) OH CO NPh [275°]. Formed from

acetone dicarboxylic ether and aniline (Emery, B 23, 3764) Yellowish plates, v sl sol alcohol.

PHENYL-AMIDIMIDO-ETHENYL-o-AMIDO-PHENYL MERCAPTAN C14H11N2S probably

 $C_*H_* <_N^N > C(NHPh) NH$ [118°] Formed together with the di-phenyl derivative by heating amido-imido-ethenyl-o-amido-phenyl-mercaptan with aniline, ammonia being evolved (Hofmann, B 20, 2254) Plates Sol. alcohol and ether

-B'H2Cl2PtCl, small needles, m sol Salts water -B'HClAuCl soluble yellow plates

Di - phenyl - amidimido - ethenyl - o - amidophenyl-mercaptan CaH15N2S which is probably C_sH₄<N C(NHPh) NPh [129°] Obtained

White silvery plates V sol alcohol as above and ether

Salts -B"H2Cl2PtCl4 dark-yellowsparinglysoluble plates $-B''H_2Cl_2Au_2Cl_6$ yellow needles PHENYL-AMIDO-JUGLONE v JUGLONE

PHENYL-AMIDO MALEIC ACID

The phenylimide NHPh C₂H C₂O₂ NPh [232°] is formed, together with the mono-anilide NHPh C₂H(CO₂H) CONHPh [176°], by boiling dibromo succinic acid or chloro- or bromo maleic or fumaric acids with aniline and water (Reissert a Tiemann, B 19, 626, Michael, B 19, 1377) The phenylimide is also formed by heating aniline with oxalacetic ether at 140° (Wishcenus a. Spiro, B 22, 3350)

PHENYL-AMIDO MALONIC ACID Anıl-*de CH(NHPh)(CO NHPh), [162°] Formed by boiling chloro-malonic acid with aniline (Conrad a Bischoff, A 209, 231) Prisms

PHENYL - AMIDO - METHENYL - AMIDO -

C₁₀H₆<0>C NHPh NAPHTHOL [168°].

Formed from benzene-azo (β) naphthol by heating with CS₂ at 250° (Jacobson, B 21, 419) Small needles, v e sol cold alcohol With HClAq at 190° it yields amido (β) naphthol, aniline, and CO₂.—Picrate [210°] Acetate [120°-130°]

PHENYL - AMIDO - METHENYL - AMIDO -

[159°] Formed from C.H. NS CCl and amline (Hofmann, B 12, 1130) Formed also by heat ing phenyl thiocarbimide with azobenzene at 270° (Jacobson a Frankenbacher, B 24, 1410) Needles, sol alcohol, insol water Decomposed by alcoholic potash at 200° into aniline and amdo-phenyl mercaptan —B'HCl —B'HAuCl₄
—B',H,PtCl₅.—B'C,H,N₅O, [222°]

Acetyl derivative [167°] Needles

PHENYL - AMIDO - METHENYL - AMIDO -

PHENOL C.H. NO NHPh [178°] Formed

by boiling C.H. NO SH with aniline (Kalckhoff, B 16, 1826) Needles, sol alcohol, ether, and

HOAc May be distilled. Weak base -B'H.PtCl. PHENYL - AMIDO - METHENYL - AMIDO -PHENYL-MERCAPTAN C, H, N, S t.e

C,H, NOCHHPh) [159°] Formed by heating chloro-phenyl-thiocarbimide with aniline (Hofmann, B 12, 1129, 15, 12). Needles

PHENYL - AMIDO - METHENYL - BENZ AMIDESULPHIM

 $C_0H_3C < N > C$ NHPh [174°] Formed by boul ing benzamidoxim (1 mol) with phenyl thiocarbimide (2 mols) for 10 hours (Koch, B 24, 894) White plates, insol water, sol alcohol, ether, and cone HClAq, insol water and alkalis Cone HClAq at 150° decomposes ... into S, H, S, amline, HOBz, and NH, Bromine forms CPh N₂S CNH.C₂H₄Br[1 4] Yields a nitrosamine [119°] and an acetyl derivative [196°], both being crystalline

PHENYL-AMIDO METHYL-ACRIDINE

 $C_{\bullet}H_{\bullet}{<}^{\rm N}_{\rm CMe} \stackrel{\rm C\ CH\ CNHPh}{\rm C\ CH\ CH}$ [216°] by heating the diacetyl derivative of mphenylene-di phenyl diamine (1 pt) with ZnCl₂ (2 pts) for 6 hours at 250° (Besthorn a Curt man, B 24, 2044) Brownish red needles, v sol alcohol sl sol ether Split up by HClAq at 250° into aniline and oxy methyl-acridine

DI PHENYL-DI-AMÍDO MĚTHYLENE-o PHENYLENE-DIAMINE

 $C_{\bullet}H_{\bullet} < NH > C(NHPh)_{2}$ [160°] Formed from di-phenyl cyanamide C(NPh)2 and o-phenylene diamine at 135° (Moore, B 22, 1635, 3190) Needles (from benzene ligroïn), insol ligroïn, v sol alcohol Yields with nitrous acid a nitros amine C.H. N2(NO)2 C(NPhNO)2[138°] Salts B",H,Cl, needles, v sol water - B"H,SO, needles, sl sol hot water -B",3H2PtCl, xaq

Di-bensoyl deriva: ve [165°] Tetra-bensoyl derivative [148°]

Tetra - phenyl - tetra - amido - di - methylene-o phenylene-diamine C_0H_1 , $N_1(C(NHPh)_s)_2 = [139^\circ]$ Formed by heating C(NPh), with o phenylene diamine at 200° (Moore) Colourless prisms vsol alcohol Split up by heat into aniline and

Salts —B",H,Cl, needles, v sol hot water -B"43H2PtCl6 -B"2H2SO4 prisms, v sol hot

water

Tetra-acetyl derivative C₆H, N₂(C(NPhAc)₂)₂ [126°] White prisms Tetra-benzoyl derivative [182°]

DI-PHENYL-DI-AMIDO-METHYLENE o PHENYLENE-PHENYL GUANIDINE

>C(NPh) >C(NHPh), [188°]. Formed

from phenylene phenyl-guanidine and C(NPh), at 210° (Keller, B 24, 2506) The homologous compound from o tolylene phenyl-guanidine melts at 200° while the corresponding body from o tolylene-p tolyl guanidine melts at 176° All three compounds crystallise from alcohol in white needles, sol benzene

PHENYL - AMIDO - METHYL - DI - ETHYL . N CEt CMe C NHPh PYRIMIDINE

Formed from chloro-methyl-di-ethylpyrimidine (derived from cyanethine) by heating with aniline and alcohol at 220° (Von Meyer

J. pr [2] 89, 274) Needles, v sol. alcohol.—
B',H,PtCl, needles
PHENYL - AMIDO - METHYL MALONIC Amsc ether CO.Et CMe(NHPh) CONH. [86°] Forred by dissolving the nitrile in cold conc. H.SO, and pouring into water (Gersen, B 19, 2965) The uttrile CO₂Et CMe(NHPh) CN [102°] is formed by heating CO₂Et CMe(OH) CN with an alcoholic solution of aniline for 24 hours at 80°. The The amic ether crystallises in white needles, sol hot water, and is converted by boiling aqueous NaOH into CH, CH(NHPh) CO, H

PHEN L-(a)-AMIDO METHYL - NAPHTHO- $C_{\bullet}H_{\bullet}Me < N > C_{1\bullet}H_{\bullet}NHPh$ PHENAZINE

[214°]. Formed by heating (1,3,4)-tolylene-diamine with benzene azo phenyl (a)-naphthylamine hydrochloride and alcohol at 140° (Eicker, B 23, 3506) 3rass-yellow needles, forming yellowish-red solutions with yellowish-green fluorescence.—B'2H2PtCl4. minute dark-red needles.

PHENYL-AMIDO - DI - METHYL-PYRIDINE $N \leqslant_{CMe}^{CMe} \stackrel{CH}{CH} > C NHPh.$ Phenyl-amido lutidme [150°] (C a E); [144°] (G a. M). (235°-238°) Obtained by heating chloro-dimethyl-pyridine with aniline at 185° (Conrad a Epstein, B 20, 165) Formed also by heating the corresponding oxy-di-methyl-pyridine (1 mol) with phenyl cyanate (1 mol.) and benzene at 100°, CO, being evolved (Goldschmidt a. Meissler, B 23, 274) White crystalline solid. sol. alcohol, ether, and dilute acids H₂SO, and a trace of HNO, it gives a bloodred colouration - *B', H, Cl, PtCl, [209°] (C a. E), [204°] (G a M), microscopic yellow needles PHENYL-AMIDO DI-METHYL-PYRROLE

NHPh N CMe CH [92°] (c 270°) Formed by heating its dicarboxylic acid, and also by the action of phenyl hydrazine on acetonyl acetone (Knorr, B 18, 1568, 22, 170) Crystalline mass, volatile with steam Insol water and alkalis, sol cone HClAq Reddens pine wood moistened with HClAq

PHENYL - AMIDO-DI - METHYL-PYRROLE. DICARBOXYLIC ACID NHPh N CMe C CO,H Needles. Got from its ether Et.A" [127°], which is formed by mixing solutions of di acetyl-succinic ether and phenyl-hydrazine in HOAc (Knorr, B 18, 304, 1568).

PHENYL (Py 1)-AMIDO-(Py 8)-METHYL QUINOLINE C.H. C(NHPh):CH [1519].

Formed by heating chloro-methyl-quinoline with aniline at 190° (Conrad a. Limpach, B 20, 953)

Prisms, al sol ether, v sol alcohol.

Phenyl-(Py 3)-amide-(Py 1)-methyl-quinoline C, H, N,. [180°] Formed by heating (Py. 3,1)-chloro-methyl quinoline with aniline (Knorr, A 236, 102) Shining plates.

B', 2H,PtOl. [235°] Yellow needles, insol Aq.

Fhenyl-(Py 1) amido-tri-methyl-quinoline

CoH,Me, C(NHPh) CH [150°]. Formed by

heating the corresponding chloro-tri methylquinoline with aniline at 185° (Conrad a. Lumph, B 21, 528). Prisms (from dilute alcohol).
PHENYL-AMIDO-METHYL-THIAZOLE

CMe.N C.NHPh. [117]. Formed by heating oxy methyl-thiazole with aniline (Hantzsch a. Weber, B 20, 8180), and by the action of chlorosectone on phenyl-thio-ures (Traumann, A 249, 262, 246). Orange-yellow prisms. You III.

47) Small white needles (from alcohol) aniline when heated with HClAq at 240°

PHENYL - AMIDO - NAPHTHALENE PHENYL-NAPHTHYL-AMINE

Di-phonyl-di-amido naphthalone Dz PHENYL-NAPHTHYLENE-DIAMINE.

Tri-phenyl tri-amide naphthalene

CH. C(NHPh) CH [1489] products formed by heating benzene azo (a)naphthylamine with aniline at 160° (Fischer a. Hepp, A 256, 251) Needles, v sol alcohol. Yields phenyl-rosinduline and a yellow substance [140°] on oxidation

Tetra-phenyl-tetra-amido-naphthalene C₁₆H₄(NHPh)₄. [191°]. Accompanies the preceding body On oxidation it yields phenylamıdo phenyl-rosindulıne, dı-phenyl-dı-amidonaphthoquinone, and a body melting at 169°.

PHENYL-AMIDO (a)-NAPHTHOQUINONE $C_{16}H_{11}NO_{2}$ i.e. $C_{6}H_{4} < \stackrel{CO}{CO} \stackrel{C}{CH} HPh$ [191*] 191¶. Formed by heating (a)-naphthoquinone with an alcoholic solution of aniline (Zincke, B 12, 1645), by boiling phenyl-amido (β) naphtho-quinone with HCl, and by the action of aniline and HOAc on oxy-(a)-naphthoquinone (Lieber mann, B 14, 1665) Long red needles, v sol. hot alcohol and ether, msol cold alkalis holic potash forms a purple solution Boiling dilute NaOH splits it up into aniline and oxy-(a)-naphthoquinone.

-CNPhH Anelede C.H. CO CNPh) CH Dı .

phenyl di-imidonaphthol [180°] Formation -1 By heating each of the naphthoquinone oxims with aniline and HOAc at 100° (Fuchs, B 8, 1023, Brömme, B, 21, 893)—2 By heating di-imido-(a)-naphthol hydrochloride with aniline at 120° (Goës, B. 13, 124) -3 By boiling (β)-naphthoquinone with an alcoholic solution of aniline (Zincke, B 15, 481) —4 By heating di bromo- (α) -naphthol with aniline (Meldola, C J 45, 157) —5 By the action of aniline and aniline hydrochloride at 100° on benzene-azo-(a) naphthol, on benzene-azo-(a)naphthylamine, and on similar bodies (Fischer a. Hepp, B 21, 679)

Properties - Orange red needles (from alcohol), forming orange solutions in bensene, acetone, and CHCl₂. Weak base Its solution in HOAc is orange when hot, but crimson when cold Hot HClAq forms a red solution Insol. alkalis Not attacked by boiling with alkalis, or by Ac₂O, AcCl, and MeI H₂SO₄ at 120° yields oxy-naphthoquinone and aniline. Zincdust and HOAc reduce it to aniline and naphthalene. Alcoholic HCl or EtBr at 150yields aniline and phenyl-amido-(a)-naphtho-HNO, forms a di-nitro- derivative quinone [143°].

Salts.—B'HCl: golden-green plates, forming a violet solution in alcohol. Decomposed by water — B'₂H₂PtCl₄: bronze needles. —
B'₂H₂ZnCl₁ bronze-green plates. — B'HI: black
needles. — B'₂H₂SO₄. — B'HNO₂. plates
De-anxiede C₁₆H₂(NPh)₂(NHPh) [159].
A product of the action of benzene-aso-(a)-

naphthylamine on aniline (Fischer a. Hepp, A.

8 I

Phenyl-amido-(\$)-naphthoquinone

C₁₆H₂O₂(NHPh) or C₆H₄<C(NPh) CH Oxy-'(β)-Naphtho-(a)-naphthogumone anilide. Prepared by quinone anilide' [245°-250°] adding aniline to an alcoholic solution of (8)-naphthoquinone (Zincke, B 14, 1494, 15, 279, Liebermann, B 14, 1664). Red needles, si sol alcohol. Weak soid Readily converted by boiling with HOAc into the isomeric phenylamido - (a) - naphthoquinone Boiling HClAq splits it up into aniline and oxy-(a) naphtho-quinone Nitrous acid passed into a solution in sloohol and HOAc forms a nitroso derivative C16H10N2O2, crystallising in red needles, and

onverted by NaOHAq into a yellow body [217°].
Salts—BaA', red needles, sl sol water—
PbA', brown pp —ZnA', —HgA', —AgA' red pp
Methyl sther MeA' [151°] Formed
from the Ag salt and MeI Yellow needles, sol alcohol and ether

Ethyl ether EtA' [104°] Prisms n-Propyl ether PrA' [104° Isopropyl ether PrA' [100°] [104°] Prisms

Di-phenyl-amido (a)-naphthoquinone C₁₀H₃O₂(NPh₂) [164²] Formed by boiling (a) naphthoquinone (5 g) with diphenylamine (6 g), alcohol, and cone HClAq (10 cc) for twenty minutes, and ppg with water (Plimpton, O J 37, 644) Needles (from alcohol)

Acetyl derivative C₂₂H₁₁AcNO₂ [173°]

PHENYL-AMIDO NAPHTHYL-UREA NHPh CO NH C₁₀H₆ NH₂. Formed from (1,2)-naphthylene diamine and phenylcyanate (Schieffelin, B 22, 1377, cf Goldschmidt, B 23, 502) Granules (from alcohol), not fused at 335° DI-PHENYL-DI-AMIDO-OIAZTHIOLE

8<C(NHPh) N [181°] Formed by adding hydrogen peroxide solution (8 pc) to phenylthio urea dissolved in dilute alcohol, acidulated with HCl (Hector, B 22, 1176) Needles, insol water, v sl sol cold alcohol Nitrous acid water, v st solt and a solt and a soluble powder, exploding at 179° Cyanogen passed into the warm alcoholic solution ppts C₁₄H₁₂N₆S, crystal lising in needles — B'HNO₅ — B'₂H₁PtCl₅ —

B'AgNO, ad granules, v sl sol hot alcohol

Acetyl derivative C, H, AcN, S [238°],

Bensoyl derivative C, H, BZN, S [238°]

PHENYLAMIDO-PALMITIC ACID

C₁₀H₃₁(NHPh)O₂ [142°] Formed by boiling a-bromo palmitic acid with aniline (Hell a Jordanoff, B 24, 942) Sol ether and benzene PHENYL-AMIDO-PHENOL OXY-DI-PHENYL-AMINE

Di-phenyl-di-amido-phenol Hydrochlor-As (C,H,(NHPh),OH)HCl [192°] Formed from azophenin, Sn, and HCl in presence of AcOH (Fischer a Hepp, 4 256, 260) Plates PHENYLAMIDO-PHENYLACETIC ACID

C, H, NO, te C, H, CH(NHPh) CO, H [164°-168°] (S) Formed by saponification of the nitrile (Tiemann a. Piest, B 15, 2030), and also by boiling brome phenyl-acetic acid with aniline and alcohol (Stöckenius, J. 1878, 779) Plates, subliming at 175° as slender white needles (T a P.). V. sl sol. water, sol alcohol -HA'HCl. nodules, decomposed by water —HA'HNO: thin needles -BaA's radiating mass

Ethyl ether EtA'. [84°]. Needles.

C.H. CH(NHPh) CONH. Silky plates, v sol. alcohol, nearly insol ligroin

Natrale O.H. CH(NHPh) CN [85°] Formed by heating an alcoholic solution of the cyanhy-drin of benzoic aldehyde with aniline at 100° Formed also by the action of KCy and HCl on benzylidene-aniline (Cech, B 11, 246) Needles or prisms, sol ether and hot alcohol

Phenyl amido-di-phenyl-acetic acid CPh_s(NHPh) CO₂H [168°] Formed by passing HCl into an alcoholic solution of benzilic acid and treating the resulting CPh,Cl CO,Et with anılıne (Klinger a Standke, B 22, 1212) Needles, v sl sol water Cone H2SO, forms r yellow solution, becoming crimson on warming

Methyl ether MeA' [107°]. Monoclinic [1150] Ethyl ether EtA'

PHENYL - AMIDO - PHENYL - ACRIDINE C.H. CPh C CH C NHPh [197°] Formed by

heating the di benzoyl derivative of m phenylene di phenyl di amine (10 g) with ZnCl, (25 g) at 250° (Besthorn a Curtman, B 24, 2045) Brownish red needles, m sol alcohol, ether, and benzene The dilute ethereal solution ex hibits a greenish fluorescence The hydro chloride is v sl sol water, and forms a red solution in alcohol

DI PHENYL - DI - AMIDO - TRI - PHENYL -CARBINOL Cal H28 N2O 1 e

CPh(OH)(C,H, NHPh), Formed by heating at phenylamine with benzyl chloride and oxidising the product with arsenic acid Formed also by heating diphenylamine with ZnCl, and oenzoyl chloride or benzotrichloride, the resulting chloride C₃₁H₂₅N₂Cl being decomposed by alcoholic NH, (Meldola, C J 41, 187) Amorphous, v sol ether, sol hot alcohol and acetone The chloride $C_{a_1}H_{a_2}N_{\underline{c}}C_{\underline{l}}$, called 'diphenylamine green,' forms bronzed granules, and, in alcoholic solution, dyes wool bluish green, and gives a dark green pp with H.PtCl, Hot H SO, con verts the chloride into the sulphonic acid

C_s,H₂,N₂SO_s, ppd by water in dark green flakes Tri phenyl tri amido tri phenyl-carbinol The chloride CCl(C_sH₄NHPh)_s, or 'diphenylamine blue,' is obtained by heating diphenylamine (1 pt) with oxalic acid (2 pts) (Willm a. Girard, D P J 221, 192, Hausdörfer, B 23, 196d) Formed also by heating pararosamiline with aniline Brownish red powder, v sol hot aniline and nitro benzene, sl sol cold alcohol

Hexa-phenyl tri-amido tri-phenyl carbinol C(OH)(C₆H₄ NPh₂)₈ Formed by the action of alcoholic NH₈ on the chloride C(C₆H₄ NPh₂)₅Cl, which is got by heating triphenylamine with COCl₂ at 190° (Heydrich, B 19, 758) White amorphous pp , forming a bluish-violet solution in H2SO4, turned blue by addition of alcohol

PHENYLAMIDO - PHENYL - ISOCROTONIC ACID C,H, CH CH CH(NHPh) CO,H [154°]. Formed by saponification of the nitrile (Peine, B 17, 2116) Minute needles, v sol. alcohol and

Amide [171°] Thin plates
Nitrile C.H.(NHPh) CN [180°] Formed
by heating CHPh CH CH(OH) CN with annine in alcoholic solution Crystalline solid, sol hos alcohol

PHENYLAMIDO-PHENYL-ETHYL-KETÜNE C,H,(NHPh) GO C,H, Homophenacylandide.

[88°] Formed from phenyl bromo ethyl ketone and aniline in alcoholic solution (Pampel a Schmidt, B 19, 2897) Yellow crystals Yields

an acetyl derivative [103°

PHENYL AMIDOPHENYL HYDRAZINE Acetyl derivative C.H. N.H. C.H. NHAc [146°] Got by reduction of C.H. N. C.H. NHAc with alcoholic ammonium sulphide (Schultz, B •Acetyl 17, 463) Glistening plates, v sol alcohol and SnCl, reduces it to aniline and shenylene diamine Conc HClAq forms a blue

ompound
PHENYLAMIDO DI PHENYL-METHANE
JH.Ph C.H.,NEPh [c 89°] Formed by heat ng diphenylamine with benzyl chloride and ZnCl₂ at 100° (Meldola, C J 41, 198) powder, v sol benzene, insol alcohol White

Di phenyl-di-amido-tri phenyl-methane J₂₁H₂₈N₂ ι e CHPh(C₆H₄ NHPh), [c 170° formed by heating diphenylamine with benzyl dene chloride, and also from diphenylamine, penzoic aldehyde, and ZnCl, (Meldola, C. J. 41, 192) White granules, v. sol. ether, yielding liphenylamine green on oxidation

Reference -- Chloro - diphenyldiamidotri

PHENYLMETHANE

PHENYLAMIDO-PHENYL METHYL PYR

IMIDINE CPh $\langle N | CMe \longrightarrow CH$ [150°-153°] Formed from chloro phenyl methyl pyrimidine and aniline (Pinner, B 18, 2852)—B'HNO, [87°]—H'HCl [240°] Long slender needles PHENYLAMIDO PHENYL PROPIONIC

PROPIONIC ACID Nutrile CH, CPh(NHPh) CN [152°] Formed by digesting an ethereal solution of acetophenone cyanhydrin and aniline at 50° (Jacoby, B 19, 1515) White prisms (from al cohol) With alcoholic hydroxylamine it yields the oxim of acetophenone Alcoholic HCl gives s trı phenyl benzene

Amide CH, CPh(NHPh) CO NH, Formed from the nititle by heating with H.SO. at 100° and pouring into water Insol water

PHENYL AMIDO TRI PHENYL PYRROLE CH CPh NHPh [232°] Formed from anhydracetophenone benzil (1 mol) and phenyl hydrazine (2 mols) in alcoholic solution at 100°

(Japp, B 21, 551, 22, 2885) Yellow needles FHENYL AMIDO TRI PHENYL QUINOX-ALINE DIHYDRIDE

 $\begin{bmatrix} 1_4^3 \end{bmatrix} C_e H_s (NHPh) < \begin{matrix} NPh.CHPh \\ N = CPh \end{matrix}$ [223°] Formed by heating di-phenyl (1,3,4) tri amido benzene with benzoin at 160° (Fischer, B 24, 722) Yellow plates, sl sol alcohol, forming a yellow solution with green fluorescence
PHENYLAMIDO PHENYL ROSINDULINE

 $\begin{bmatrix} 4 \\ 2 \end{bmatrix} C_0 H_1 (NPh) \ll_{NPh}^{N-C} C \frac{C}{CH C(NHPh)} > C_0 H_1$ [192°] Formed by heating benzene-azo (a)naphthyl - amine with aniline and benzene (Fischer a. Hepp, A 262, 237) Formed also by exidation of (1,2,3,4) tetra phenyl-tetra amidonaphthalene (Fischer a Hepp, A 256, 252) Bronzed plates, forming a dark-green solution in cone HadO, becoming reddish-violet on dilution -B'HCl bronzed plates

OTRI - PHENYL - TRI - AMIDO - DI-PHENYL-

TOLYL-CARBINOL

C(OH)(Q.H. NHPh) (C,H. NHPh) Anthre blue,

Lyons blue Triphenylrosaniline Formed, to gether with mono and di phenyl rosaniline by heating rosamiline acetate or benzoate with aniline (Girard a De Laire, D P J 162, 297, Hofmann, Pr 12, 578, 13, 9) Prepared by heating rosaniline (1 pt) with aniline (10 pts) and a little benzoic acid, dissolving in alcoholic NH_s, and pouring into water White pp, insol water, v sol alcohol, m sol ether Yields di phenyl amine on distillation. Reduced by zinc and HCl to tri phenyl tri amido di phenyl tolyl methane or tri-phenyl leucaniline (Hofmann, C R 57, 25) —C₃₈H₃₂N₃Cl Spirit soluble blue Opal blue Small brassy crystals, insol water and ether, sl sol alcohol Becomes brown at 100° Left with coppery lustre on evaporation of the alcoholic solution Blue dye $-(C_{18}H_{22}N_3),SO_4$ v sl sol alcohol The salts of mono phenyl-ros aniline dye violet, those of di phenyl rosaniline Tri phenyl rosaniline yields a bluish violet mono, di, tri, and tetra sulphonic acids, the Na salts of which are v sol water and dye wool blue (Nicholson, Bulk, B 5, 417)

The mono and di sulphonic acids are known as Nicholson's or Alkali blue, the tri sulphonic

acid as Soluble blue

Reference — TRI CHLORO TRI PHENYL-BOSANIL TNF.

TRI PHENYL AMIDO PHOSPHIDE OXIDE PO(NHPh), [208°] Formed from POCl, and aniline (Michaelis a Soden, A 229, 334) sided plates, insol water, sl sol ether and alco hol, v sol HOAc Yields PO(NHC, H, Br.), crys HO PO(NHPh)₂ [197°] may be got by treating annine with ether and POCl₄, followed by water

TRI-PHENYL TRI-AMIDO-PHOSPHINE SULPHIDE PS(NHPh), $[153^{\circ}]$ Formed from annihne and P₂S₃ below 150° (Knop, B 20, 3352)

Monoclinic crystals

PHENYLAMIDO PROPIONIC ACID

C₂H₁₁NO₂ to CH₃ CH(NHPh) CO₂H Formed by saponification of the nitrile or of the ether (Tiemann a Stephan, B 15, 2036, Nastvogel, B 22, 1792, 23, 2010) Plates (from hot water), sol alcohol. May be sublimed Yields a hydrochloride decomposed by water, and a white silver salt

Ethyl ether EtA' (272°) 8G 198 1060 Formed by heating α bromo propionic ether with

aniline on the water-bath

Formyl derivative CH, CH(NPh CHO) CO,H Prepared from NaNPh(CHO) and a-bromo-propionic ether (Paal a Otten, B 23, 2597) Large prisms, sol alcohol and ether —BaA', aq white powder Acetyl derivative CH, CH(NAcPh) CO.H.

[143°] Plates (from hot benzene), sl sol cold water —NaC₁₁H₁₂NO₂3aq plates —EtA' (294° 298°) Oil, formed from sodium acetanilide and a bromo propionic ether

Amade CH, CH(NHPh) CONH. [141°]

Plates, sol alcohol and hot water

Analide CH, CH(NHPh) CO NHPh [126°].

Needles, v sol hot water

Netrele CH, CH(NHPh) CN [92°] Formed by heating the cyanhydrin of acetic aldehydd with aniline (T a S) White plates, sol also hol and ether Weak base —B'HCl [86°]

Isomerides v Amido-Phenyl Propionic acid.

Di-phenyl-di-amido-propionio acid. Netrile CH(NHPh), CH, CN [113]. Formed by heating CHO CH, CN with amiline for 20 hours at 310° (Chautard, A. Ch. [6] 16, 180) Needles, v. sol. water and benzene —B'HCl.—B',H,PtCl.; small yellow needles, v sol. water

Reference. - TRI-BROMO PHENYL-AMIDO-PROPIO-

NITRILE

PHENYL-8-AMIDO-PROPYL-PHTHALIM-IDE C.H. O.O. N CH. CHMe.NHPh Formed from β-bromo-propyl-phthalimide and aniline (Seitz, B 24, 2631) Yellow needles Decomposed by HCl at 1906 into phthalic soid and propylene-diamine

Phenyl-γ-amido-propyl-phthalimide C.H. C.O. N CH. CH. CH. NHPh [89°] Formed by heating γ -bromo-propyl phthalimide (54 g) with aniline (37 g) at 150° (Goldenring, B 23, 1168) Yellow crystals (from boiling ligroin) Split up by heating with HCl, yielding phenyltrimethylene-diamine

PHENYLAMIDO-PROPYL-UREA

NHPh C₂H₂ NH CO NH₂ [98°] Formed by warming C₂H₄(NH₂Cl) NHPh with potassium cyanate at 100° (Goldenring, B 23, 1173) Rose-coloured needles, v sol alcohol. Decomposes at 120° in NH, and phenyl-trimethylene-

PHENYLAMIDO-PYROTARTARIC ACID CO.H CH. CMe(NHPh) CO.H Andido methylsuccesse aced [102°] Obtained by saponification of its ether (Schiller-Wechler, B 18, 1037) White needles (containing aq), v sol. hot water and alcohol, nearly insol ether. Its solution in KOHAq is colourless NH, Aq forms a violet solution.-CuA" aq -CuA"NH, green pp -HA"HCl aq white crystalline solid

Ethyl ether of the mono-amide CO_Et CH_OMe(NHPh) CONH_ [125°] Formed by digesting CO_Et CH_CMe(OH) CN with anilme in ether, dissolving the resulting compound CO_Et.CH_2.CMe(NHPh) CN in H_SO_4, and pouring into water Plates, sol hot water Converted into the imide by heating with water, alcohol, acids, or alkalis

NHPh.CMe CO>NH. r150°1. Formed as above. White prisms, sol alcohol and hot water. Yields a nitrosamine $C_{11}H_{11}(NO)N_2O_2$ [178°], an acetyl derivative [285°], and a benzoyl derivative [190°

CH, CO NHPh ČMe CO>NMe Methylimide Formed from the imide, MeI, MeOH, and KOH Yields a nitrosamme Prisms C₁₂H₁₂N₂O₂ crystallising in needles [147°] Forms also C₁₂H₁₂MeN₂O₂Me₂PtCl₂, which is all sol Aq

Phenylemide NHPh.CMe CO>NPh Socalled 'n-Phonyl-a-keto-y-oxy-\beta-a1-demethyl-\betaanilido-a-tetra-hydropyridine carboxylic lactone.' [181°] A product of the action of heat on phenylamido-pyrotartaric acid (Reissert, B. 21, 1885; Anschütz, A 261, 140) Prisms Its acetyl derivative [169°] (from alcohol) forms tabular crystals.

Mono-antitde C.H. (NHPh)(CO.H)(CONHPh). [150°]. Got by boiling the phenylimide with NaOHAq Forms Forms with nitrous soid a compound melting at 204°.

Acetyl derivative of the anhydride NAcPh CMc CO 0 [186°] Got by boiling the acid with AcCl (Anschütz) Tables, v sol. chloroform, al sol ether

Acetyl derivative of the anilide C.H.(NAcPh)(CO.H)(CONHPh) [141°] Formed from the preceding body by the action of aniline

on its ethereal solution Prisms PHENYL-(Py 8) AMIDO-QUINOLINE

O'H' CH'OH'OH Phenyl-quinolmamme [98°] (above 860°). Formed by heating (Py 5)-chloro-quinoline with aniline (F iedla ider a. Weinberg, B. 18, 1532) White plates

Reference — Bromo-Phenyl-Amido Quinolime. PHENYL - AMIDO - QUINOLINEQUINONE -CH C(NHPh) C CH CH C(NPh) CO C N CH ANILIDE Formed by adding excess of aniline to an alcoholic solution of CH CCl Co H,N brand, B 21, 2986) Long needles (from alcohol and HOAc), forms a deep-blue solution in dilute HClAq — *B'HCl. dark-golden needles — Acetate [199°] Bronzed needles, decomposed by water — B'C.H.N.O.. Coppery needles PHENYLAMIDO-QUINONE Dianiled

Dianilide C.H. (NPh), (NHPh)[1 4 2] [230°] Formed from azophenine and HOl at 160° (Fischer a Hepp, A 256, 261) Reddish-brown needles, forming a blue solution in conc H.SO.

Di-phenyl di-amido-quinone

Quinone dianilede C.H.O. (NHPh). [1 4 2 5] Quinone dianilide Formed, together with hydroquinoue, by boiling quinone with an alcoholic solution of aniline (Hofmann, Pr 18, 4, Wichelhaus, B 5, 851, Zincke, B 16 1556, Knapp a Schultz, A 210, 178) Formed also by heating chloro-quinone with aniline and HOAc (Niemeyer, A 228, 332) and by strongly heating aniline with dioxyquinone (Nietzki a Schmidt, B 22, 1655) Small violet plates, sol HOAc and aniline, nearly msol. alcohol May be sublimed Conc H2SO4 forms a reddish violet solution

Antlide C.H.(NHPh), NPh. [208°]. A product of the action of aniline on quinone in HŌAc (Zincke a Hagen, B 18, 785), on o-nitrophenol (Fischer a Hepp, A 262, 247), and on quinone phenylimide (Bandrowski, M 9, 415) Reddish-brown needles, forming a blood-red solution in H2804 On warming with alcoholic H_2SO_4 it yields $C_6H_2(\ddot{N}HPh)(OEt) < V_{\ddot{N}Ph}$ coholic potash forms C18H14N2O2 crystallising in red needles [192°], v sol. alcohol, and forming a green solution in H.SO. Di-anilide C.H. (NHPh), (NPh), is Aso-PHENINE

DI-PHENYL - DI - p - AMIDO - QUINONE DI-CARBOXYLIC ETHER

C_e(NHPh)₂O₂(CO₂Et)₂[1.4 2 5 8 6] Di anilido-quinone di-carboxylic ether. [246°]. Formed by the action of aniline in alcoholic solution upon p-di-chlore-quinone-di-carboxylic ether C_cCl_cO_s(CO_sEt)_s (Hantzsch a. Zeckendorf, B 20, 2) Glistening garnet-red crystals.
PHENYLAMIDO-SUCCINIO ACID 1812)

CO.H.CH.CH(NHPh) CO.H. Phenylaspartic acid. [182°] Formed by boiling bromo succinia

acid with aniline, and by the decomposition of an aqueous solution of acid maleate of amline (Anschutz a. Wirtz, Am 9, 248, A 289, 140) Small crystals—H.A"HOL monoclinic prisms.

Phenylimide C.H.(NHPh) C.O.NPh. »[211°]. Formed by heating maleic anhydride with aniline. Formed also, together with the dianilide C.H. (NHPh) (CONHPh), [206°], by heating asparagine with aniline (Pinti, G 14, Small needles (from alcohol) Yields a amine [180°] Alcoholic NH, forms the nstrosamine [180°] amide-amilide [200°]. The diamlide yields a nitrosamine [190°]

Imelle. [1586] Formed from bromo-succinimide and annline (Kusseroff, A 252, 158)

Ethyl ether C.H.(NHPh)(CO.Et). (214°) Oil, forming a crystalline sulphate

Di-phenyl-di-amido-succinic acid

CO₂H ČH(NHPh) CH(NHPh) CO₂H. ſc 190° Formed by saponifying its other, which is formed by heating di-bromo succinic ether with aniline in alcohol (Lopatine, C R 105, 230; Gorodetzky a. Hell, B 21, 1796) Plates (from HOAc), nearly insol. water, m. sol alcohol

Ethyl ether Et.A" [150°] Needles. Forms with Br a hexa-bromo-derivative [104°]

PHENYL-AMIDO-SULPHO-BENZOIC ACID C.H.(NHPh)(SO.H) OO.H [1 2 4] Formed from bromo sulpho benzoic acid and alcoholic aniline (Rescher, B 24, 3802) Plates — (NH_Ph)HA" needles (from water) Plates -BaA" 5aq

PHENYL-AMIDO-THIAZOLE C.H.N.S i.s. 8.O(NHPh) CH_CH>N [126°] Formed by the action of phenyl-thio-ures on di-chloro-di-ethyl ether (Hantzsch a Traumann, B 21, 940, A 249, 47) Small white needles, al sol water, v sol alcohol.

PHENYLAMIDO-TOLUQUINONE C., H., NO. i.e. C.H.Me(NHPh)O. [145°] Formed in small quantity, together with di-phenyl-amido toluquinone and its phenylimide, by the action of aniline in alcohol and HOAc on toluquinone (Hagen a Zincke, B 16, 1559) Red needles (from dilute alcohol)

Anilide C.H.Me(NHPh) [1519].

Formed by reducing the anilide of di-phenyl-diamido-tolugumone with SnCl. and HOAc (Fischer

a. Hepp, 4 256, 259) Red needles Di-phenyl-di-amide-toluquinone

Formed as above C.HMe(NHPh),O. [238°] Brown needles (from alcohol), forming a red solution in H.SO.

Antide C.HMe(NHPh), NPh. [1780]

Tolugumons treamileds. Formed as above, and also by heating nitroso-o-cresol (tolu-quinone mono-oxim) (1 pt.) with aniline (4 pts.) and aniline hydrochloride (2 pts.) (O. Fischer a. Hepp, B. 21, 678) Brown plates with bluish lustre, sol hot alcohol—B'HI. Brownish needles.— B',H,PtCl,.-B'HBr dark-green needles.

PHENYLAMIDO ROLYI-AGETIC ACID

C,H,NO, 4.e. (1:3]O,H,Me.CH(NHPh) CO,H.
[189°]. Formed by saponifying its nitrile, which is mady by heating O,H,.CH(OH)CN with aniline in ether at 100° (Bornsmann, B 17, 1471) Silvery plates (from dilute alcohol), v sol. hot Aq.

Amade O,H,N(CO.NH.) [128°]. Plates.

Nétréle O,H,N.ON. [95°]. Plates.

PHENYL AMIDO-TOLYL KETONE

Phthalyl derivative [202°] C.H. CO C.HMeN C.O. C.H. Formed. together with an isomeride [160°], by heating the phthalyl derivative of p-toluidine with benzoyl chloride and ZnCl. (Fröhlich, B 17

2672), Dimetric crystals, v sol. hot HÓAc DI-PHENYL-AMIDO-p-TOLYL-UREA [1 8 4] O.H.Me(NH.) NH OO NPh. [187° Formed by reducing the nitro-compound in alcoholic solution with SnCl, and HCl (Lellmann a. Bonhöffer, B 20, 2123) Needles, solidifying at 165°-170°, and melting a second time at 220°-260°, yielding diphenylene and tolylene-urea at 800°

PHENYLAMIDO ISOVALERIC ACID

CHMer-CH(NHPh) COrH S. 7 at 100°. Formed from bromo isovaleric acid and aniline (Duvillier, A Ch. [5] 21, 446, C R 88, 425) Scales (from hot water), v sol alcohol and ether— B'HCl needles, decomposing at 100°-110°
DI-PHENYL-#-DI-AMIDO-0-XYLENE

C_cH₄(CH₂NHPh)₂ [172°] Formed by boiling o-xylylene bromide with an alcoholic solution of aniline (Leser, B 17, 1825) Small colourless plates Weak base.

PHENYLAMINE . ANILINE.

Diphenylamine C,H,N s.s. NHPh. Mol. w 169 [54°] (302°) (Graebe, A 288, 362). S.V 2084 (Lossen, A 254, 72), 2038 (Ramsay) Formation—1 By the dry distillation of

tri-phenyl-rosaniline (Hofmann, A 132, 168) -2 By heating aniline (3 mols.) with aniline hydrochloride (2 mols.) for thirty hours at 210 (De Laire, Girard, a. Chapoteaut, Bl [2] 7, 360 C R 74, 811, 1254, Merz a. Weith, B 5, 268; 6, 1511) —8 By distilling 4-di-phenyl-urea or tri-phenyl-urea (Michler, B 9, 715) -4 By heat ing phenol with aniline-zinc-chloride to 250° (Mers a Weith, B 13, 1298) -5 By heating a mixture of aniline, phenol, and SbCl. at 150°-160° (Buch, B 17, 2639)

Preparation.—By heating aniline with aniline hydrochloride at 230° and treating the warm

product with HClAq followed by water

Properties - Monoclinic plates Forms a colourless solution in H2SO4 changing on warming to blue, when a trace of nitrous or nitric acid is present (test for nitrous acid in H_*SO_4 : Kopp, B 5, 284, Piutti, A 227, 181) A solution in conc. H_*SO_4 (5 c c) is coloured blue by shaking with a solution (1 c c.) containing nitric acid (test for nitric acid Muller, Bl [8] 2, 670). With PbO, and alcoholic HOAc it gives a bright olive green colour (Lauth, C R 111, 9 Pioryl chloride forms dark-red needles 975).

ricryl chloride forms dark-red needles of NHPh₂SC₆H₄(NO₂)₂Ol [66°] (Hers, B 28, 2540)

Reactions—1 When passed through a redhot tube it yields carbazole, aniline, benzene,
and NH₄ (Graebe, A 174, 177)—2. COCl₂ forms
NPh₂COCl (Michler, B 8, 1684)—8 ClCO₂Et
forms NPh₂CO₂Et [72°]—4. Chlorius in presence of I yields NH(C,H,Cl.), and finally C,Cl. (Ruoff, B 9,1488) —5 Browses and I yield tetra, hexa-, octo-, and deca- bromo-diphenylamines (Gessner, B. 9, 1505).-6. Alkaline KMnO, yields orsales soid, a resin, and a substance $C_1H_1M_1$ orystallising in yellow needles [176°–180°], which yields quinone on oxidation by MnO, and cone. HNO, may be reduced to p-phenylene-di-phenyl-diamine [186°], and yields a (hexa?)-bromoderivative [248°] (Bandrowski, M 7, 375, 8,475, 9,418) -7 Yields acridine on warming with AlCla and chloroform HOAc and ZnCl, give methylacridine, and other acids act in like manner — 8. PCl, and ZnCl₂ at 250° yield C₁₂H₁₀NPO, a white powder (Michaelis, B 21, 1504, A 260, Acrolein in alcoholic solution forms (C₁₂H₁₉N)₂C₂H₄, an amorphous powder, sol chloroform, capable of combining with Br (Leeds, B 15, 1158, A C J 4, 32) -10 Heated with oxalic acid it gives diphenylamine blue -11 Heated with sulphur it gives imido-di-phenyl sulphide 12. HNO, forms a hexa-nitro- derivative which decomposes carbonates

Salts -B'HCl needles (from alcohol), decomposed by water —B'H SO₄. [125°] Insole ther and benzene, decomposed by water —Benzene sulphonate [117°] —Toluene p-sulphonate [64°] (Norton, Am. 10, 129, 140).

140)

Formyl derivative C12H11NO se NPh, CHO [74°] Formed by heating di phenylamine with oxalic or formic acid (Willm Formed by heating di a. Girard, B 8, 1195) Insol water, sol benzene and alcohol Yields acridine on heating with ZnCl,

Acetyl derivative NPh, Ac [103°] Plates (from ligroin), sol. hot water Yields NPh Bz on heating with BzCl (Pictet, B 23, 3013) followed by water forms an acid C1.H1.ClNPO, aq and an oil converted by alcoholic NH, into C_sH₃₀N₄O [186°] (Claus, B 14, 2367)

Thro-acetyl derivative NPh. CS CH. [111°] Formed by heating u-di phenyl-acetamidine with CS₂ at 100° (B) Tables, sl sol

water, v e sol ether

Bensoyl derivative NPh,Bz [177° Formed from diphenylamine and BzCl (Hof mann, A 132, 166, Bernthsen, A 192, 18, 224, 12, Wallach, A 214, 235), and also by the action of Ph.N COCI on benzene in presence of AlCl. (Lellmann a Bonhöffer, B 19, 3231) Trimetric needles, abc = 9501 824 Sl sol ether and water, m sol hot alcohol

p-Toluyl derivative. [155°] Dr-methyl-bensoyl derivative

{4 8 1}C_eH₃Me₂CONPh₂ [186°] Formed from o-xylene, NPh. COCl, and AlCl, (Lellmann, B

20, 2119)
Netrosamene NPh. NO [66 5°] Yellow
four-sided tables (from benzene-alcohol) (Witt,
Franker A 190, 174) Yields B 8, 855, Fischer, A 190, 174) Yields azophenine when heated with aniline and aniline hydrochloride at 120° Its hydrochloride heated with p bromo-aniline at 80° yields tetra-bromo-azophenine C₁₈H₁₅Br₄N, [248°] (Ikuta, A 243, 285) On heating with aniline it yields PhN.O.H.NH., PhN, NHPh, and diphenylamine by heating with alcoholic HCl it is converted into nitroso-diphenylamine.

Tri-phenyl-amine O18H18N 8.6 NPh, Mol w 245. [127°]. Formed by dissolving Kor Na in ani line or diphenylamine and digesting the product with brome-benzene (Merz a Weith, B 6, 1514, Heydrich, B. 18, 2156) Monoclinic crystals (from ether), $a \ b.c = 991 \ 1$: 412, $\beta = 88^{\circ} \ 88' \ 81$. hot alcohol, m sol benzene. Does not form salts. AcCl at 100° gives a greenish substance. Cold conc. H₂SO₂ gives a violet colour, changing to blue. Benzotrichloride and ZnOl₂ give a green colouring matter on heating A solution in

HOAc is coloured green by a little HNO. Chlorine and I yield N(C,Cl,), and finally C,Cl.

(Ruoff, B 9, 1483)

Isomeride of triphenylamine. CieHisN Got by distilling the compound of cinnamic aldehyde with (NH.)HSO_s (Gössmann, A 100,57) Liquid, volatile in a current of H at 140°-150°, sl sol. water, v sol alcohol and ether Forms unstable salts, decomposed by water and alcohol EtI yields B'Etl, whence moist Ag O yields oily B'EtOH, while platinic chloride forms while B',Et,PtCl,.—B',H,PtCl, monometric crysta's
—B',PtCl,

References - AMIDO, DIBROMO, BROMO-DI NITRO-, CHLORO, CHLORO NIT.10-, NITRO, and OXY, DIPHENYLAMINE

DIPHENYLAMINE SULPHONIC C12H11NSO, 16 NHPh C6H4 SO2H [200°]. Formed, together with the disulphonic acid, by heating diphenylamine with H.SO, at 160° (Merz a Weith, B 5, 283, 6, 1512) Formed also by heating NPh.HSO, H. at 190° for 2 hours Formed (Vignon, C R 107, 263) Crystalline mass, becoming blue in air -KA' plates -BaA', plates,

bi sol water —PbA'₂ nodules, sl sol water Diphenylamine disulphonic acid

NH(C₂H₂SO₂H)₂.—BaA'₂2aq nodules, v e sol water Hydrolysed by HClAq at 200° (Girard,

Bl [2] 23, 2)

Diphenylamine disulphonic acid

C.H. (NHPh)(SO.H),[124] Formed from bromobenzene disulphonic acid and aniline in glyceria (Fischer, B 24 3807) V e sc1 Aq -BsA" 3aq Anrilde C.H.(NHPh)(SO2NHPh), [2220].

Yellowish crystals, insol water

Triphenylamine trisulphonic acid N(C4H4 SO3H)3 Formed by adding powdered triphenylamine to fuming H.SO, at 60° (Herz, 95 pc alcohol), v e sol water, insol alcohol
PHENYL-AMMELINE v Cyanuric acid in

the article Cyanic acid

PHENYL-AMYL-AMINE O ANYL ANILINE D1-phenyl-isoamyl-amine NPh2CaH11 (330°-840°) Formed from diphenylamine, amyi alcohol, and HCl (Girard, Bl [2] 28, 2) Gives a blue colouring matter when heated with oxalic acid and H2SO,

DIPHENYL-DI-ISOAMYL-TETRAZINE NPh(C_sH₁₁) N_s NPh(C_sH₁₁) [86 5°] Formed from phenyl isoamyl hydrazine in ether and HgO (Michaelis a Philips, A 252, 286) Yel

lowish crystals

PHENYL-AMYLENE OHPh OHPr 215°) Formed by passing bromine vapour into amyl benzene at 150° and distilling the product (Schramm, A. 218, 892) Yields a dibromide

Phenyl-isoamylene OHPh OHPr (201°) at 787 mm S.G. 12 878 Made in like manner from isomyl-benzene (S) Yields a dibromide

Phenyl-amylene CHPhEt CH CH. S G 2 846 Formed by boiling CHPhEt.C₂H₁Br with water or alcoholic potash (Dafert, M 4, 621). Liquid, readily converted into the poly meride C.H., (208°-212°), S.G. 22 96°, 10 2 (calc 10 1).
DI-PHENYL-AMYLEME DIKETONE

(C.H. CO CH.CH.), CH. aw-Di bensoyl-pentane. [68°]. Formed by the action of boiling KOH is MeOH on CH2Bz CH2CH2CH2 CHBz CO2Et, which is get from sodium benzoyl-acetic ether and phenyl bromo-butyl ketone (Kipping a W H Perkin, jun, O. J 55, 849) Long col needles, insol. water, m. sol. cold alcohol Long colourless

Di-oxim [176°]. Small needles PHENYL-ISOAMYL-HYDRAZINE

NPh(C_sH₁₁)NH₂ (260°) Formed from isoamyl bromide and sodium phenyl-hydrazine in benzene (Michaelis a Philips, A 252, 284) Reduces warm Fehling's solution. Ac₂O yields NPh(C₅H₁₁) NHAc [125°] crystallising in scales DI-PHENYL-ANYLIDENE DISULPHONE

CEt₂(SO₂Ph), [181°] Formed from NaOH, CH₂(SO₂Ph), and EtI (Fromm, A 253, 168) Formed from NaOH,

Orystalline, v sl sol. hot alcohol.

PHENYL AMYL-KETONE C.H. CO CHEt (230°) at 710 mm Formed by boiling di ethylbenzoyl-acetic acid with dilute alcoholic potash (Baeyer a Perkin, jun, B 16, 2131, C J 45, 185) Thick oil.

Phenyl amyl ketone C.H. CO CH, Pr (240°) at 720 mm Formed by heating isobutyl-benzoylacetic ether with dilute alcoholic potash (W H Perkin, jun, a Calman, C J 49, 166) Oil, with

aromatic odour

PHENYL AMYL KETONE CARBOXYLIC ACID C₈H, CO CH_CH_CH_CH_CH_CH_CO_H [82°] Formed by boiling the compound CH_Bz CH_CH_CH_CHBz CO_Et with KOH in M60H (Perkin a Kipping, C J 55, 350) Plates (from light petroleum), or needles (from water) Yields an oxim [75°] AgA' amorphous pp Isomerides, vo. i p 482

PHENYL ISOAMÝL OXIDE C.H. O C.H.

Got from phenol (Cahours, A 78, 227)
PHENYL - ISOAMYL - PHOSPHINE (225°) DÍ OXIDE P(C₄H₃)₂(C₅H₁₁)O [97°] Formed from PPh₂C₅H₁₁I and Ag₂O (Michaelis a Soden, A 229, 317) Needles, sol water and ether

DI-PHENYL-ISOAMYL-THIO-SEMICARB-C₅H₁₁ NPh NH CS NHPh AZIDE Formed from phenyl isoamyl-hydrazine and phenyl thiocarbimide (Michaelis a Philips, A

252, 285) Yellow needles

PHENYL-AMYL-THIO UREA C12H18N2S + 6 NHPh CO NH CH, CMe, [136°] Formed from the corresponding amylamine and phenyl-thiocarbimide (Freund a Lenze, B 23, 2868)

PHENYL AMYL UREA C₁₁H₁₁N₁O te NHPh CO NH CH₂CMe₃. [155°] Formed from phenyl cyanate and the corresponding amylamine in alcoholic solution (Freund a Lenze,

B 23, 2867, 24, 2158) White needles
PHENYL - ANGELIC ACID C, 1H, 0, s.c.
CHPh CHEt CO, H Mol w 176 [104°] Formed by heating benzoic aldehyde with sodium butyrate and Ac.O at 100° (Perkin, O J 31, 391, 32, 661, 35, i36, Slocum, A 227, 53) Formed also by heating benzoic aldehyde with butyryl chloride at 125° (Fittig, & 153, 364) Needles, v sol after having been fused —BaA' needles, m

sol hot water — CaA', — AgA' white pp Chlorids C₁₀H₁₁ COCL Oil Amids C₁₀H₁₁ CONH. [128]

Phenyl-angelic acid CHPh OH CH, CH, CO, H Formed from OHPh CH CH CO.H by reduction with sodium-amalgam (Perkin, Basyer a. Jackson, B. 18, 122) Liquid.—AgA' white pp

Phenyl-angelic acid CHPh CH CHMe CO.H. (05°) Formed by boiling the dibasic acid. [110 5°] CHPhBr CH(CO,H) CHMe CO,H with water (Penfield, A 216, 128), and by distilling CHPh CH(CO,H) CHMe (Fitting a Liebmann, A 255, 262) Plates (from water) -BaA'2 aq. needles, v sol water

Phenyl-angelic acid CHPh CMe CH, CO, H. [113°] Formed by distilling the lactonic acid $CHPh < CMe(CO_2H) > CH_2$ (F s. L). tables, sl sol water -BaA'2 groups of needles, sol. water

rhenyl angelic acid Nitrile C.H. CHPh CN (c 265°) Forme Formed by heating phenyl-acetonitrile with NaOH and allyl iodide (Buddeberg, B 23, 2068) Oil, converted by NaOEt and benzyl chloride into the benzyl

PHENYL-ANTHRACENE C₂H₁t & C₁H₂Ph. [158°] (417°) Formed by heating phenyl-anthranol with zinc-dust (Baeyer, A 202, 61), and by the action of chloroform and AlCl. on benzene (Friedel, Crafts, a Vincent, Bl [2] 40, 97; A Ch. [6] 1,495) Leaflets (from alcohol), forming solutions with blue fluorescence Reduced by P and HI to a crystalline dihydride [120°], which is oxidised by CrO, in HOAc to phenyloxanthranol

PHENYL ANTHRANOL C. H 1.0 1.6

 $C_eH_4 < \stackrel{CPh}{<} C(OH) > C_eH_4$ [141°-144°] Formed by dissolving tri phenyl methane o-carboxylic acid in H2SO, and ppg with water (Baeyer, A 202, 57). Golden needles, sol hot alcohol Its ethereal solution shows greenish yellow fluorescence

[166°] Acetyl derivative Golden

needles, turned red by conc KOHAq

Reference -DI CHLORO-PHENYL ANTHRANOL PHENYL-ARSINE v vol 1 p 319 The sulphides PhAsS [152°] and Ph₂As₂S₃ [130°] have been prepared by Schulte (B 15, 1956)

PHENYL AZIMIDO-COMPOUNDS V AZIMIDO-COMPOUNDS

DI - PHENYL - TETRAZINE C14H12N4 t.s. NPh < N CH N NPh [180°] Mol w 240 by Raoult's method (calc 236) Formed by the action of chloroform and alcoholic potash on phenyl hydrazine (Ruhemann, C J 53, 850, 55, 243) White needles (from alcohol) HNO, yields C, H, (NO,)N, [above 300°] H, SO, forms C₁,H₁₁(SO₂H)N₄ Bromine gives C₁,H₁₁BrN₄ [220°], C₁₄H₁₆Br₂N₄ [181°], and C₁₄H₂Br₃N₄, decomposing at 224°

needles -B',H,PtCl,-Salts -B'HCl B'MeCl. [244°] Needles — B', Me, PtCl, — [214°] Yellow needles, v sol alcoh L

PHENYL AZO- COMPOUNDS v Azo- com-POUNDS

PHENYL-TETRAZOLE CPhHN, Le

N≪N CH Formed by heating its carboxylic acid [138°] at 155° (Bladin, B 18, 2907) Heavy oil, v sol. alcohol and ether Explodes when strongly heated Sol acids, but reppd on dilution

PHENYL-TRIAZOLE CARBOXYLIC ACID OH NPh [184°]. Formed by boiling phenyl-hydrazine dicyanide NH2NPh CCy NH i with formic acid and heating the resulting formyl derivative with alcoholic potash (Bladin, B 23, 3788). Silvery plates (from water).

Methyl ether MeA' [118°] Prisms.

Phenyl-triszole dicarboxylic acid

CO,H C N O CO,H Formed by oxidising phenyl-methyl-triazole carboxylic acid with alkaline KMnO, (Bladin, B 23, 3785) The free analine Kanid, (Blatin, B 25, 9189). The free acid is unstable, readily changing to the preceding acid. The acid K and Na salts also readily give off CO₂—CuA" 4aq blue needles—Ag₂A" 4aq? Bulky white pp

Methyl ether Me₂A" [167°] Needles

Ethyl ether Et,A" [82°] Needles Dı phenyl-triazole carboxylic acid

CPh≪N C CO, H Formed by saponification of the nitrile (Bladin, B 22, 797) Crystals (containing EtOH), decomposing at 172°-182° sol. alcohol, m sol ether -CuA'2 -AgA' white

Methyl ether MeA' [159°] Needles Ethyl ether Eth' [165°] Needles Ethyl ether EtA' [165°] Needles Netrele C.N.Ph. CN [156 5°] Formed from phenyl-hydrazine dicyanide, alcohol, and benzoic

aldehyde Needles, v sol benzene
Am: de O.N.Ph. CO.NH. [196°].

H₂O₂ and KOHAq needles (from water) Plates (from alcohol) on

Amidozim C,N,Ph, C(NOH) NH, [214ግ, Formed from the nitrile and hydroxylamine (Bladin, B 22, 1752) Prisms (from alcohol) Yields an acetyl derivative [177°] which yields $C_sN_sPh_sC < N O > CMe$ [153°], and a benzoyl de rivative [180°] which yields in like manner C₂H₂Ph₂ C NOPh [206°].—B'HCl: crystal

PHENYL-TETRAZOLE CARBOXYLIC ACID $N \leqslant_N^N \overset{NPh}{C} CO_2H$ [188°]. Got by sapon fication of its nitrile, which is formed by the action of nitrous acid on phenyl-Lydrazine dicyanide (Bladin, B 18, 2907) Colourless needles, v sol alcohol -- KA' plates, v sol water -- CuA', 2aq -AgA' colourless crystalline pp

Methyl ether MeA' [116°]. Plate Ethyl ether EtA' [74°]. Needles Amide CN,Ph CO NH, [168°] F Formed from the nitrile by treatment with hydrogen peroxide. Crystals, sl sol cold water

Amidoxim CN Ph C(NOH) NH. Formed from the nitrile and hydroxylamine aldebyde Needles, v sol benzene (Bladin, B 22, 1755) Scales, v st. sol water.

Am:de O,N,Ph,CO.NH, [196°]. Formed from the nitrile by the action of dilute (8 p a.) derivative [206°], both crystallising in needles

END OF THE THIRD VOLUME.